

**PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
VOLUME 2C - DATA EVALUATION AND INTERPRETATION REPORT
HUDSON RIVER PCBs REASSESSMENT RI/FS**

February 1997



For

**U.S. Environmental Protection Agency
Region II
and
U.S. Army Corps of Engineers
Kansas City District**

**Volume 2C
Book 3 of 3**

TAMS CONSULTANTS, Inc.

The CADMUS Group, Inc.

Gradient Corporation

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APPENDIX A

DATA USABILITY REPORT FOR PCB CONGENERS HIGH RESOLUTION SEDIMENT CORING STUDY

A.1 INTRODUCTION

The usability of data relates directly to the data quality objectives of the environmental investigation (Maney and Wait, 1991; USEPA, 1993, 1994). The Hudson River PCB congener chemistry program required sophisticated, high resolution gas chromatography analyses with stringent quality control criteria. In addition, various inorganic and physical parameters were analyzed to define the chemical context within which the PCB congeners exist. This approach was necessary to delineate the concentration of PCB congeners within the context of geochemical and biological processes occurring in the river.

TAMS/Gradient selected a total of 90 PCB congeners as target congeners based on their significance in environmental samples and the availability of calibration standards at the start of the program. In addition, Aquatec obtained qualitative and quantitative information for an additional 36 PCB congeners (non-target congeners) from each sediment sample analysis using relative retention time information detailed in the literature, and more recently verified with actual standards. Certain target congeners are of particular importance in evaluating geochemical and biological processes within the Hudson River sediments. These are the 12 "principal" target congeners, which consist of BZ#1, 4, 8, 10, 18, 19, 28, 52, 101, 118, 138, and 180. The focus of this report will be on the usability of the analytical data for these 12 principal congeners.

This report serves as an overall evaluation of the PCB congener analyses performed for the Hudson River high resolution sediment coring study. The evaluation is based on the assessment of data quality relative to the objectives of the study. The report will first provide a synopsis and assessment of the field sampling, analytical chemistry and data validation programs, and then evaluate data usability for all 126 congeners analyzed, with particular emphasis on the 12 principal

target congeners. A data usability report assessing the non-PCB chemical and physical analyses for the high resolution sediment samples is provided in Appendix C.

A.2 FIELD SAMPLING PROGRAM

TAMS/Gradient designed the high resolution sediment coring study to examine long-term trends in PCB transport, release and degradation by an examination of the sediment record. TAMS/Gradient describe the high resolution sediment collection program, sampling procedures, analytical protocols, and quality control/quality assurance requirements in the "Phase 2A Sampling and Analysis Plan/Quality Assurance Project Plan - Hudson River PCB Reassessment RI/FS" (TAMS/Gradient, May 1992, referred to in this report as the Phase 2A SAP/QAPP). TAMS/Gradient collected cores over a 200-mile length of the Hudson River using either hand coring, gravity coring, or piston coring techniques. Co-located cores at each site were required to provide sufficient sediment for all chemical and physical testing. Once the cores were returned to shore, the sampling team extruded and aliquoted sediments from the cores in a manner described in the Phase 2A SAP/QAPP. For most samples, this procedure involved taking 2 centimeter (cm) slices from the top of the core for four intervals, and then removing 4 cm slices from the remainder of each core. The sampling team aliquoted each slice into appropriate containers and submitted the samples to a contract laboratory for analysis. A summary of the subsampling and analysis scheme is provided in Figure A-1.

During the process of defining data quality objectives for the high resolution sediment coring sampling study, TAMS/Gradient acknowledged that only a limited amount of sediment could be obtained from 2 cm and 4 cm core slices. This affects the number of analyses that can be performed per slice, as well as the detection limits for each analysis. TAMS/Gradient determined that increasing the length of the core slices would cause valuable sediment dating information to be lost. TAMS/Gradient considered this approach to be unacceptable because one of the main purposes for conducting the high resolution sediment coring study was sediment dating. Consequently, TAMS/Gradient decided to collect four cores at each site rather than two cores to obtain sufficient sediment mass. The problem with collecting co-located samples, particularly for sediments, is the potential lack of representativeness (homogeneity) between each core. TAMS/Gradient decided to collect multiple co-located cores in order to obtain all desired analyses at acceptable detection limits,

with the belief that co-located core homogeneity would be acceptable. A discussion on field sampling precision and representativeness is provided in the data usability section of this report.

Scientists from TAMS, Lamont Doherty Earth Observatory (formerly Lamont Doherty Geological Observatory), and Rensselaer Polytechnic Institute (RPI) performed sampling for the high resolution sediment coring program from August 23, 1992 to November 6, 1992. The sampling team collected a total of 495 sediment samples from 28 primary sampling stations in areas of relatively continuous sedimentation of fine-grained material. Aquatec allocated these samples into 30 sample delivery groups (SDGs). In addition, the sampling team collected core tops from several additional locations throughout the Hudson River in May and August to October of 1992. RPI dried and archived core tops (0-2 cm) from these cores for eventual PCB congener analysis. Aquatec analyzed a small subset of the archived core tops (A-cores) for PCBs. The TAMS/Gradient Program Quality Assurance Officer (QAO) conducted a field sampling audit on September 9 and 10, 1992 to assess compliance of the sampling procedures with the Phase 2A SAP/QAPP. The audit findings indicate that the sampling program was being conducted in a technically acceptable manner consistent with the Phase 2A SAP/QAPP (Wait, 1992).

A.3 ANALYTICAL CHEMISTRY PROGRAM

A.3.1 Laboratory Selection and Oversight

TAMS/Gradient retained a number of analytical laboratories to perform the analyses required for this program. To verify that the selected laboratories had the capacity, capabilities, and expertise to perform sample analyses in strict accordance with the specified methodologies, each qualifying laboratory underwent an extensive audit by TAMS/Gradient's senior chemists. TAMS/Gradient retained the following three laboratories to perform high resolution sediment sample analyses for the Hudson River RI/FS program: Aquatec Laboratories, a division of Inchcape Testing Service located in Colchester, Vermont; Lamont Doherty Earth Observatory (LDEO) located in Palisades, New York; and Rensselaer Polytechnic Institute Department of Earth and Environmental Science located in Troy, New York. USEPA Special Analytical Services (SAS) contract laboratories, ATEC Associates, Inc. located in Indianapolis, Indiana; GeoSea Consulting, Ltd. located in Vancouver,

British Columbia; and Chemtec Consulting Group Inc., located in Englewood, New Jersey, were also retained through the USEPA SAS procurement process. Aquatec was the sole analytical laboratory which conducted the PCB congener analyses for the entire program.

TAMS/Gradient conducted routine laboratory audits during the high resolution sediment coring study to verify compliance of the laboratories contracted by TAMS/Gradient (Aquatec, LDEO, and RPI) with the Phase 2A SAP/QAPP requirements. TAMS/Gradient did not perform audits of the USEPA SAS laboratories.

Unique requirements of the PCB congener method necessitated refinements of previously published methods. In conjunction with these changes, Aquatec conducted Method Detection Limit (MDL) studies and Extraction Efficiency (EE) studies for the sediments to evaluate the adequacy of the methods. To conduct these studies, TAMS/Gradient collected seven replicate Hudson River sediment samples. For the MDL studies, TAMS/Gradient collected the samples upstream from the zone of major PCB contamination. TAMS/Gradient collected samples used for the EE study from within the zone of major PCB contamination. A synopsis of the MDL/EE studies is provided in a TAMS/Gradient memorandum dated December 29, 1993 (Cook, 1993). The TAMS/Gradient Program Quality Assurance Officer oversaw and approved the method refinements through out the process.

A.3.2 Analytical Protocols for PCB Congeners

The method used by TAMS/Gradient for the determination of PCB congeners in Phase 2A is a program-specific method based on NYSDEC's Analytical Services Protocol Method 91-11 (NYSDEC, 1989) for PCB congeners. Appendix A4 of the Phase 2A SAP/QAPP describes procedures for the calibration, analysis, and quantitation of PCB congeners by fused silica capillary column gas chromatography with electron capture detection (GC/ECD). The method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. Aquatec extracted sediment samples with hexane, and performed applicable cleanup procedures prior to analysis by GC/ECD, as detailed in Appendix A3 of the Phase 2A SAP/QAPP. Aquatec analyzed hexane extracts for PCB congeners on a dual capillary-column GC/ECD, as detailed in Appendix A4 of the Phase 2A SAP/QAPP and identified PCB congeners using comparative

retention times on two independent capillary columns of different polarity. Aquatec used calibration standards for each target congener to define retention times. In addition, Aquatec routinely analyzed Aroclor standards and mixtures of Aroclor standards to verify identification and quantification of the primary calibration standards. Due to the non-linear nature of the ECD over any significant calibration range (for this project 1 to 100 ppb in extract), Aquatec generated the calibration curves used for quantitation from a quadratic weighted least squares regression model where the correlation coefficient is greater than 0.99 (McCarty, 1995; USEPA, 1986 - Method 8000B, proposed 1995 update). For each PCB congener which elutes as a single congener on each GC column, Aquatec reported the result as the lower of the two values. Although this quantification scheme is compliant with USEPA CLP guidelines for dual-column analyses (USEPA, 1991), it may introduce a slight low bias when calculating homologue and total PCB sums. TAMS/Gradient compared data in the database relative to absolute results on both columns and found the bias was usually negligible, and on a worst-case basis, may be 2% to 10% low. For situations where coelution occurred on one column, Aquatec quantitated the result from the column not displaying coelution. If only coelution results were available, Aquatec performed a calculation to decipher concentrations using response factors derived by Mullen (1984). For the 12 principal congeners, BZ#19, 28, 52, and 118 eluted as a single congener peak on both GC columns. BZ#1, 4, 8, 10, 18, 138, and 180 eluted as a single congener peak on one column and coeluted on the other column. BZ#101 coeluted on both columns and was always reported with BZ#90.

Approximately 10% of all samples analyzed by GC/ECD also underwent additional analysis using a GC-ion trap detector (ITD) as an additional means of confirming PCB congener identifications, as detailed in Appendix A5 of the Phase 2A SAP/QAPP. When possible, Aquatec selected samples with the highest concentrations of PCB congeners for confirmation analysis by GC/ITD. Usually, Aquatec performed two GC/ITD analyses per SDG, even if congener concentrations were minimal throughout the SDG.

At the start of the Phase 2A sampling and analysis program, TAMS/Gradient and Aquatec selected 90 target PCB congeners. These target congeners are listed in Table A-1 and identified by BZ number (Ballschmiter and Zell, 1980). TAMS/Gradient and Aquatec based the selection of these 90 PCB congeners on their significance in environmental samples and the commercial availability of calibration standards. TAMS/Gradient referred to PCB congeners for which calibration standards

were available as "target congeners". To verify that congener response for these calibration standards were reproducible over time, TAMS/Gradient examined calibration data from November 1992 and October 1993. TAMS/Gradient found temporal consistency to be acceptable on both GC columns (Bonvell, 1994a).

The high resolution column chromatography techniques employed by Aquatec produced acceptable PCB resolution for numerous congeners not contained in the target congener calibration standards. Thus, TAMS/Gradient decided during method refinement to report approximately 50 additional PCB congeners. The laboratory identified these additional PCB congeners based upon the relative retention times reported in the published literature (Mullen, 1984; Schulz, 1989; Fischer and Ballschmiter, 1988, 1989). Aquatec calibrated these additional "non-target" congeners using the calibration curve for target congener BZ#52. Aquatec chose BZ#52 because it elutes as a single congener peak in the middle region of the chromatogram for both GC columns and is a major component of Aroclor 1242, the Aroclor anticipated in Hudson River samples. Using additional congener calibration standards which became commercially available by August 1993, Aquatec performed analyses to verify and refine the historical relative retention times, and to determine individual congener calibration parameters. These analyses confirmed a majority (36) of the historical non-target congener relative retention times. For all analyses performed prior to August 1993, the results for 14 non-target compounds not confirmed by this analysis, TAMS/Gradient considered unusable and deleted from the database. A review of project data indicated that the 36 confirmed non-target congeners represent a significant percentage, up to 25%, of the total PCB mass. Therefore, TAMS/Gradient decided to include the non-target congener results to calculate homologue and total PCB masses in the Hudson River. Omission of these non-target congener results would have resulted in a significant low bias in the resulting calculations for homologue and total PCBs. Thus, 36 non-target congeners are included in this report, as shown in Table A-1. Since the non-target congener results were to be included in the calculations of homologue and total PCB mass, TAMS/Gradient applied an individual correction factor to each congener's results based on the analysis of the additional congener standards. The application of these correction factors served to minimize the uncertainty associated with quantitation of non-target congeners. A series of TAMS/Gradient memoranda describe the method for deriving these calibration correction factors (Bonvell, 1993a,b,c). A listing of the derived calibration correction factors is provided in a TAMS/Gradient memorandum (Bonvell, 1994b).

To establish a method of quantitating total Aroclor concentrations from PCB congener data, Aquatec performed duplicate analyses of seven Aroclor standards (1016, 1221, 1232, 1242, 1248, 1254, 1260). TAMS/Gradient defined the quantitation of an Aroclor for this program as the sum of all congeners present in the standard Aroclor mixture at a concentration greater than 0.1% of the total Aroclor mass. In this manner, TAMS/Gradient then compared the percentage of the total mass represented by the detected target and non-target congeners greater than 0.1% of the Aroclor mass was then compared to the actual concentrations of each Aroclor standard. The results produced the following mass yields for the seven Aroclor standards: Aroclor 1016=93.3%, Aroclor 1221=86.8%, Aroclor 1232=91.0%, Aroclor 1242=90.6%, Aroclor 1248=89.2%, Aroclor 1254=95.8%, and Aroclor 1260=87.0%. Thus, in each case, the 90 target and 36 non-target congeners represented more than 87% of the original Aroclor mass. For those Aroclors most important to the Hudson River based on General Electric's reported usage (Brown *et al.*, 1984) these congeners represented better than 90% of the Aroclor mass (*i.e.*, Aroclors 1242, 1254, and 1016). A further discussion of the results of the Aroclor standards analyses is presented in Section 4.3 of the main body of this report.

A.4 DATA VALIDATION

An essential aspect of understanding the uncertainties of the Phase 2 sediment data is understanding the significance of the qualifiers associated with the results. Each result has an associated qualifier. Qualifiers denote certain limitations or conditions that apply to the associated result. Initially, the analytical laboratories applied qualifiers to the results, and then the data validators modified the qualifiers, as necessary, based on the established validation protocols. Data reporting and validation qualifiers direct the data users concerning the use of each analytical result. TAMS/Gradient used two sets of qualifiers in the database, one set for PCB congener data, and a second set for non-PCB chemical and physical data. Aquatec developed an extensive list of data reporting qualifiers to be applied to the PCB congener data. The list is based on standard USEPA qualifiers used for organic analyses, with additional qualifiers provided to note unique issues concerning PCB congener analysis, *e.g.*, the quantitation scheme. The data reporting qualifiers for PCB congener data, as applied by Aquatec, are defined in detail in Table A-2. Qualifiers for non-PCB data are discussed in Appendix C.

During validation, the validators made modifications to the data qualifiers which are reflected in the database. CDM Federal Programs Corporation and their subcontractors, under a separate USEPA contract, performed data validation for the high resolution sediment coring study. Validation procedures employed by CDM for GC/ECD analyses are detailed in Appendix A6 of the Phase 2A SAP/QAPP, and validation guidelines for GC/ITD analyses are provided in Appendix A7 of the Phase 2A SAP/QAPP. TAMS/Gradient devised the validation procedures to reflect the data quality objectives of the program, as well as to conform with USEPA (1988, 1992a) standards as appropriate. USEPA Region II concurred with these method-specific validation protocols. In addition, TAMS/Gradient designed comprehensive data validation templates to facilitate consistency of approach and actions during validation. Prior to validation of the PCB data, Gradient conducted a training workshop to aid CDM in properly performing the validation. Gradient reviewed and commented on the initial CDM validation reports and provided real-time QA oversight. USEPA Region II (Lockheed ESAT) revalidated data for 13 high resolution sediment coring samples to verify that CDM had performed the validations properly. Lockheed ESAT noted no significant problems.

The initial data validation efforts for the high resolution sediment core samples and water column samples were completed in December 1994. The results were subsequently incorporated into the TAMS/Gradient database and available for review in March 1995. However, by April 1995, it became clear that the validation results differed markedly but randomly from the unvalidated data. Upon further investigation, the project staff at TAMS identified the source of some of these differences as the result of incorrect data validation procedures largely pertaining to blank corrections. Specifically, it was found that blank samples were sometimes incorrectly associated with environmental samples and blank values were transcribed incorrectly among validation records, among other concerns. These problems were found to be extensive enough that USEPA, in agreement with TAMS/Gradient, decided to have both the entire high resolution sediment coring and the water-column monitoring PCB analysis data validation program redone to minimize manual data manipulation and transcription (*e.g.*, Garvey, 1995). TAMS developed a computer spreadsheet macro for data validation in July 1995. This macro electronically applied blank qualification criteria (*i.e.*, the "B" qualifier) to the electronic data files using an algorithm developed from the data validation procedures. These files were then used to generate the standard data validation forms incorporated in the validation packages. Subsequent to the electronic validation, CDM reviewed all

data for blank qualifier assignment before approving the data validation packages. As a result of this review, minor changes in the macro had to be made to handle unusual data packages (*e.g.*, extra congeners reported). Using the data validation macro, CDM completed the revalidation of the high resolution sediment coring and water column PCB samples in September 1995.

As an overall assessment of data quality, the TAMS/Gradient Program QAO reviewed pertinent aspects of the sampling and analysis program (*e.g.*, historical data, implementation of sampling protocols, laboratory performance) relative to the data quality objectives. Decisions on data usability sometimes overrode data qualification codes, as justified in this report. All qualifier changes made by the TAMS/Gradient Program QAO, as reflected in this data usability report, are noted in the final database (code Y in QA Comment field of database). For the high resolution sediment coring study, TAMS/Gradient Program QAO modified 3033 qualifiers out of 62,426 PCB congener data records as a result of data usability issues, representing 4.9% of the data. Specifically, TAMS/Gradient Program QAO unrejected data for two reasons: 1) octachloronaphthalene (OCN) was deemed to be an unacceptable surrogate standard (see Section A.5.2); as such, TAMS/Gradient Program QAO unrejected any sample results rejected solely due to poor OCN recoveries, and 2) CDM rejected certain positive BZ#18 detects due to poor dual column precision. The TAMS/Gradient Program QAO changed the rejection qualifier (R) to presumptively present (N). The TAMS/Gradient Program QAO based this decision on the routine presence of BZ#18 in historical sediment samples containing PCBs, and the consistent PCB congener pattern distribution present throughout the Hudson River sediments. Both the preponderance of BZ#18 retention time data and BZ#18 identification verification by GC/ITD for most ITD-confirmed samples warrants inclusion of this principal congener in the database.

A.5 DATA USABILITY

A.5.1 Approach

Most previous studies of PCB chemistry in Hudson River sediments have focused on the concentration of specific Aroclors, total PCBs and/or the distribution of PCB homologues. The current assessment of PCB fate and distribution in the Hudson River required TAMS/Gradient scientists to implement sophisticated equilibrium chemistry and transport modeling studies requiring concentration ratios of certain PCB congeners. Of the 90 target and 36 non-target congeners, 12 target congeners are of particular importance. The usability of these "principal" congeners is key to the high resolution sediment coring study.

Principal congeners will be employed in the following studies by the data users:

- Molar dechlorination product ratio - The molar sum of BZ#1, 4, 8, 10, and 19 are compared to the molar sum of all 126 congeners analyzed. This ratio is then compared to a similar index for Aroclor 1242 to assess, calculate, and evaluate the extent of dechlorination.
- Transport modeling - BZ#4, 28, 52, 101, and 138 are considered independently as compounds modeling PCB transport.
- Aroclor 1016 and 1242 - BZ#18 is used to estimate the potential contribution of Aroclor 1016 and 1242 to Hudson River sediments.
- Aroclor 1254 - BZ#118 is used to estimate the potential contribution of Aroclor 1254 to Hudson River sediments.
- Aroclor 1260 - BZ#180 is used to estimate the potential contribution of Aroclor 1260 to Hudson River sediments.

Thus, 12 principal congeners (BZ#1, 4, 8, 10, 18, 19, 28, 52, 101, 118, 138, and 180) are the focus of this usability report. However, the remaining target and non-target congeners have important implications to the high resolution sediment coring study. TAMS/Gradient used these congeners to calculate the concentrations of total PCBs, PCB homologues, and Aroclor mixtures, as well as for congener pattern analysis.

A.5.2 Usability - General Issues

The data quality objectives for the Hudson River high resolution sediment coring study required the development of a sensitive program-specific gas chromatography method. Available standard agency methods were not adequate to achieve the congener-specific identifications and detection limits needed for the project. TAMS/Gradient based the method utilized on a modified NYSDEC ASP Method 91-11 (1989) protocol encompassing information published in the literature, as well as in-house research conducted by Aquatec. This research included Method Detection Limit (MDL) studies and Extraction Efficiency (EE) studies conducted in accordance with USEPA (1984, 1986) guidance. During the course of these studies, and the inception of the high resolution sediment coring analytical program, TAMS/Gradient and Aquatec noted various nuances to the methods that required refinement. As such, TAMS/Gradient and Aquatec made modifications to some of the original protocols. The remainder of this section discusses some of the more significant changes, and their ramifications.

A.5.2.1 Identification of Non-Target Congeners

At the beginning of this program, Aquatec identified non-target congeners based on historical relative retention times reported in the literature. In August 1993, Aquatec analyzed calibration standards for each of the non-target congeners. Using these additional calibration standards, Aquatec performed analyses to confirm historical relative retention times. Though these analyses verified a majority of the historical non-target congener relative retention times, some of the historical relative retention times used to identify non-target congeners did not match the relative retention times determined by the analyses of the non-target congener standards. TAMS/Gradient deleted fourteen non-target congeners from the database for all analyses performed prior to August 1993 due to these

unconfirmed identifications. The 14 non-target congeners deleted were: BZ#35, 39, 46, 100, 104, 130, 131, 132, 134, 162, 165, 173, 176, and 179. Aquatec identified and confirmed these 14 congeners based on the current laboratory-derived relative retention times for samples analyzed during and after August 1993. Therefore, the results for these 14 non-target congeners will remain in the database for all samples analyzed during and after August 1993. Use of these non-target congener data should be limited since they are not consistently available for all data sets. If a situation arises where information for the deleted non-target congeners is critical to a data user, an in-depth review of the chromatograms and re-calculation of the concentrations could potentially produce usable results for some of these congeners.

A.5.2.2 Quantitation of Non-Target Congeners

The laboratory originally quantitated non-target congeners using the calibration curve determined for BZ#52. Since the non-target congener results were to be included in the calculations of homologue and total PCB mass, TAMS/Gradient desired a more accurate method of quantifying the non-target congeners. Aquatec analyzed calibration standards for the non-target congeners in September 1993, and again in April 1994, for the determination of congener-specific response factors. Based on this information, TAMS/Gradient calculated correction factors for each non-target congener and applied these to the laboratory data within the database (Bonvell, 1994b).

A.5.2.3 Re-calculation of Some PCB Congener Results

From August 1992 to July 1993, Aquatec observed that the relative retention times of congener compounds were changing on the SB-octyl-50 GC column. The shifts in relative retention times did not effect the target compound identification except for BZ#187 and 128. This specific identification problem became apparent from the results of a blind performance evaluation sample. In the case of BZ#187 and 128, their original identification on the SB-octyl-50 analytical column showed BZ#128 eluting before BZ#187. Over the course of eight months, the two congeners merged together as one peak, then became resolved again, only BZ#187 now eluted before BZ#128. When the two congeners resolved, Aquatec assumed that each congener eluted in the same order as previously indicated, which was incorrect. To determine the effects of the shifts on the non-target congeners, Aquatec analyzed individual non-target congener standards. From these data, Aquatec

discovered that the initial identification of non-target PCB congener compounds obtained from Ballschmiter's research was inconsistent with this study's SB-octyl-50 analytical column results. During the review of the elution order of PCB congeners on the SB-octyl-50 column, Aquatec also discovered that BZ#91 was misidentified. TAMS/Gradient and Aquatec corrected the misidentification of BZ#91 and the other affected congeners.

Aquatec finalized the proper identification of non-target PCB congeners in November 1993. In March 1994, TAMS/Gradient instructed Aquatec to review all PCB congener data analyzed from September 1992 to July 1993 to rectify possible misidentifications. These corrections also necessitated changes in the PCB congener database. All data initially entered into the database have been validated without consideration to the changes discussed herein. Due to the GC column problem, Aquatec changed some records and TAMS/Gradient flagged those records with a "K" to facilitate comparison of original and changed records. A secondary validation of the changes has not been performed. However, the identification changes made are not expected to adversely effect the overall validity of the data. Some possible problems to be aware of include the analytical status of calibration curves and check standards for BZ#91 for the entire time period, and BZ#187 and 128 from March 17, 1993 through July 1993. Another possible problem was 'B' flags. The 'B' flag was used to indicate method blank contamination. Requantitation of results has changed the 'B' qualifier status in some cases.

A.5.2.4 GC Column Change

Initially, Aquatec used a HP-5 (or RTx-5) column and a SB-octyl-50 GC column for PCB congener analyses. In November 1993, Aquatec obtained new SB-octyl-50 columns for pending analyses of Phase 2 biological samples. Each of the new SB-octyl-50 columns showed signs of column degradation resulting in severe peak retention time shifts. Due to the concern that an acceptable SB-octyl-50 column would not be obtainable, TAMS/Gradient solicited approval from USEPA Region II for a replacement column, Apiezon_L. TAMS/Gradient was concerned about data comparability for the overall program, but had no alternative. USEPA Region II concurred with the replacement of the SB-octyl-50 column with the Apiezon_L column in December 1993. The Apiezon_L column was selected for the following reasons:

- The Apiezon_L column phase is similar to the SB-octyl-50 column phase.

- The Apiezon_L column provides PCB congener separations similar to the SB-octyl-50 column.
- The PCB congener retention times on the Apiezon_L column are more stable than on the SB-octyl-50 column.
- The NYSDEC analytical laboratory performing Hudson River PCB congener analyses was using the Apiezon_L column successfully for fish samples.

In February 1994, Aquatec performed a comparison study for the two column sets, HP-5/SB-octyl-50 and HP-5/Apiezon_L (Cook, 1994). Aquatec analyzed four Phase 2 pilot fish samples on both the HP-5/SB-octyl-50 column combination and also the RTx-5/Apiezon_L column combination. The PCB congener results compared well qualitatively and quantitatively with few exceptions. The results for BZ#15 and 37 were consistently 2 to 10 times higher on the SB-octyl-50 column pair. Data users are cautioned that the results for BZ#15 and 37 reported through March 1994 and the same congeners reported after March 1994 are not comparable due to differences in the method of quantitation. For example, comparisons of sediment data between the high resolution sediment coring study and the low resolution sediment coring study are not appropriate for BZ#15 and 37.

A.5.2.5 Lower Column Concentration Bias

The USEPA CLP protocol requires that for dual column GC analyses, the lower of the two values from each column will be reported (USEPA, 1991). TAMS/Gradient incorporated this same quantitation scheme into this program. This quantitative method may introduce a slight low bias when calculating homologue and total PCB sums. TAMS/Gradient determined that this bias was usually negligible, and on a worst-case basis, may be as much as 2% to 10% low. Therefore, the data user should consider these totals as usable, but estimated values, due to the uncertainties of the individual results which are summed to form these values.

A.5.2.6 Surrogate Spike Compound

At the inception of the high resolution sediment coring study, TAMS/Gradient and Aquatec employed two surrogates, tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN). Aquatec noted soon after the program began that OCN recoveries were a problem. For many of the sediment samples, recoveries were less than 10% and sometimes 0%, although the TCMX and matrix spike/matrix spike duplicate results for these same samples were usually acceptable. Reextraction and reanalysis of the same samples produced similar results. The purpose of surrogate spike analyses is to evaluate the performance of the extraction procedure. TAMS/Gradient and Aquatec determined that OCN was an inappropriate surrogate for this program. Research by Aquatec suggests that OCN was breaking down to heptachloronaphthalene and hexachloronaphthalene. During the validation process, CDM rejected data that had OCN recoveries below 10%. During this data usability assessment, the TAMS/Gradient Program QAO considered these results to be usable and changed the R qualifier to a J qualifier (estimated results) for any result solely rejected due to poor OCN recoveries.

A.5.2.7 Confirmation by GC/ITD

Aquatec analyzed approximately 10% of all samples analyzed by GC/ECD by GC/ITD to provide an additional mechanism to verify congener identification and, as a secondary objective, quantitation of congeners. The ITD is not as sensitive as the ECD (approximately an order of magnitude less sensitive); therefore, when possible, samples with the highest concentration of PCBs were selected for GC/ITD confirmation. Although this may result in a program bias for only confirming high concentration samples, the overall effect does not impair data usability.

In addition, there is the potential for some quantitative bias associated with the GC/ITD results relative to the GE/ECD results. Aquatec quantified each congener detected in the GC/ITD analysis using an average response factor per level of chlorination rather than using response factors determined specifically for each individual congener. As such, potential bias, which will vary for each congener within a chlorination homologue group, is present with the GC/ITD results. Since the ITD method was not designed to be a primary quantitative tool, some variations in quantitative results were expected. TAMS/Gradient considered quantitative differences between the GC/ITD and

GC/ECD results less than a factor of five acceptable, while differences greater than five times were considered unacceptable and associated results rejected.

A.5.3 Usability - Accuracy, Precision, Representativeness, and Sensitivity

TAMS/Gradient established a quality assurance system for this program to monitor and evaluate the accuracy, precision, representativeness, and sensitivity of the results relative to the data quality objectives. These are all important elements in evaluating data usability (*e.g.*, USEPA, 1992b, 1993). Accuracy is a measure of how a result compares to a true value. Precision indicates the reproducibility of generating a value. Representativeness is the degree to which a measurement(s) is indicative of the characteristics of a larger population. Sensitivity is the limit of detection of the analytical method.

This section will evaluate each of these parameters for the high resolution sediment coring study. TAMS/Gradient assessed accuracy using holding times, instrument performance and calibrations for both the GC/ECD and GC/ITD, internal standard performance for the GC/ITD, surrogate criteria for both the GC/ECD and GC/ITD, spike recoveries, matrix spike/matrix spike duplicate recovery results, and compared identification results. TAMS/Gradient assessed precision by comparing matrix spike and matrix spike duplicate results. (A performance evaluation [PE] sample was submitted with the water column samples. The results of the PE sample are discussed in Appendix B.) TAMS/Gradient evaluated representativeness by comparing field duplicate results, and assessed sensitivity using blank results and the sample-specific quantitation limits achieved.

Comparability and completeness are two other important data quality attributes. Comparability expresses the confidence with which data are considered to be equivalent (USEPA, 1992b). Comparable data allowed for the ability to combine the analytical results obtained from this study with previous Hudson River studies. An in-depth discussion of data comparability is provided in Chapter 3 of the main body of this report. In addition, Gauthier (1994) has provided Aroclor translation procedures for Hudson River capillary column GC data relative to previous packed column GC studies. Completeness is a measure of the amount of usable data resulting from a data collection activity (USEPA, 1992b). For this program, a 95% completeness goal was established. A

discussion of completeness for the high resolution sediment coring study is provided in the conclusions section of this report.

A.5.3.1 Accuracy

Accuracy was evaluated based on a number of factors, including holding times; instrument performance; calibration; internal standard performance; surrogate spike recoveries; matrix spike/matrix spike duplicate recoveries; and congener identification. These factors are discussed below:

- **Holding Times**

Exceedance of holding times may indicate a possible loss of PCB congeners due to volatilization, chemical reactions, and/or biological alterations. Due to the persistent nature of PCBs, only severe exceedance should be considered deleterious to quantitative accuracy. For the sediment samples, TAMS/Gradient established an extraction holding time of 7 days from sampling, followed by an analysis holding time of 40 days from extraction.

Aquatec missed initial extraction holding times for only one sediment sample. However, Aquatic reextracted 26 sediments sample past holding times. TAMS/Gradient considered data for all these samples estimated. However, there were a significant number of sample extracts that Aquatec analyzed outside of holding times. A summary of holding time exceedances are provided in Table A-3.

CDM appropriately qualified all data affected by missed holding times as estimated (G). CDM qualified few samples for missed extraction holding times (5.9% of samples); and for those few samples, the exceedances were not excessive. CDM noted significant analytical holding time violations for many samples (16.7% of samples). In most cases, this was a direct result of Aquatec encountering preparation and/or analytical problems requiring reextraction and reanalysis of the samples, or dilution of extracts with congener concentrations above the calibration range. As large as some of these exceedances were, there should be no deleterious consequences to data quality. Aquatec has routinely demonstrated the stability of all PCB congener standards in solvent is at least

six months. Therefore, the TAMS/Gradient Program QAO considered all data qualified as estimated due to both extraction and analytical holding time violations to be usable.

- **GC/ECD Instrument Performance**

Adequate chromatographic resolution and retention time stability throughout an analytical sequence are essential attributes for qualitative identification of congeners on a GC. TAMS/Gradient defined criteria for congener resolution and retention time windows in the Phase 2A SAP/QAPP. For the SB-octyl-50 column, resolution must be greater than 50% between BZ#5 and 8, 40 and 41, 183 and 185, and BZ#209 and OCN. On the HP-5 column, resolution must be greater than 25% between BZ#4, 10 and TCMX, and between BZ#31 and 28. Resolution must be greater than 50% between BZ#84 and 101/90, and between BZ#206 and OCN. Aquatec initially established retention time windows for both columns to be 0.3% relative to the average initial calibration retention times for all target congeners and surrogates.

CDM noted the only congener calibration standard coelution problems for BZ#5 with BZ#8 were on the HP-5 column. This occurred for five SDGs (171158, 172467, 172592, 170805, and 172624), with resolution ranging from 30% to 49%. The 50% resolution criteria established by TAMS/Gradient for BZ#5/8 for this program was optimistic. Since 25% resolution was acceptable for other congeners on the HP-5 column, the TAMS/Gradient Program QAO did not consider these exceedances to be serious and they do not affect data usability. Only one SDG (167440) had any significant number of exceedances for retention time criteria. However, all retention times were within an expanded retention time window of 0.4% (as agreed to by EPA Region II), and therefore, did not affect identification.

Regarding sensitivity, for SDG 169803 Aquatec obtained no response for BZ#1 (a principal congener) on the SB-octyl 50 column during the entire analytical sequence, hence CDM estimated (G) and considered presumptively present the positive results for BZ#1 in all samples for this SDG. This data is usable as a result of the documentation of its historical presence in Hudson River sediments.

- **GC/ITD Instrument Performance**

Verifying proper GC/ITD performance required evaluating GC column resolution, ion trap detector sensitivity, and ion trap calibration. The GC resolution criteria required baseline separation of BZ#87 from BZ#154 and BZ#77. The ion trap sensitivity requires the signal/noise ratio for m/z 499 for BZ#209 and m/z 241 for chrysene-d₁₂ to be greater than 5. For ion trap calibration, the abundance of m/z 500 relative to m/z 498 for BZ#209 must be 70% but 95%. TAMS/Gradient noted no significant ITD performance problems for samples analyzed during the high resolution sediment coring study.

- **GC/ECD Calibration**

Instrument calibration requirements were established to verify the production of acceptable quantitative data. Initial calibrations using 5-level standard concentration curves demonstrate an instrument is capable of acceptable performance prior to sample analysis. The IC criteria is 20% relative standard concentration error (%RSCE) for monochlorobiphenyl and 15% RSCE for all remaining PCB congeners, and a correlation coefficient 0.995. Continuing calibration standards document maintenance of satisfactory performance over time. The only initial calibration problem of any significance was with BZ#2. For six SDGs (171177, 172592, 172148, 170805, 172624, and 166425), BZ#2 was not detected in the low-level standard (5 ppb in extract), which required raising the detection limit to the next lowest standard concentration (15 ppb in extract). For three SDGs (167188, 169031, and 167188), the correlation coefficient for BZ#2 was slightly below the requirement of 0.995, thus requiring all related BZ#2 data for those SDGs to be qualified as estimated (G). TAMS/Gradient noted no significant continuing calibration problems.

- **GC/ITD Calibration**

The initial calibration criteria for acceptable quantitative data for GC/ITD analyses required percent relative standard deviations (% RSD) of the congener relative response factor (RRF) to be less than 20%. For continuing calibration, the RRF for each congener must be within 20% of the mean calibration factor from the 5-level calibration at the beginning and end of each calibration sequence.

For the high resolution sediment coring study, TAMS/Gradient noted no significant GC/ITD calibration problems.

- **GC/ITD Internal Standard Performance**

To demonstrate the stability of the ITD, internal standard performance criteria were monitored. Internal standard area counts must not vary by more than 30% from the most recent calibration or by more than 50% from the initial calibration. In addition, the absolute retention time of the internal standard must be within 10 seconds of the retention time in the most recent calibration, and ion abundance criteria must be met for chrysene-d₁₂ and phenanthrene-d₁₀. For the high resolution sediment coring study, TAMS/Gradient noted no significant internal standard problems.

- **Surrogate Spike Recoveries**

Aquatec spiked surrogate compounds into all sediment samples prior to extraction to monitor recoveries. Recoveries may be indicative of either laboratory performance or sample matrix effects. For the high resolution sediment coring study, Aquatec used TCMX and OCN as surrogates. As previously discussed, OCN did not perform properly as a representative surrogate, therefore, only TCMX recoveries provide useful information. Therefore, the TAMS/Gradient Program QAO considered data rejected solely because of poor OCN recoveries to be usable as estimated values. These sequences are found in the QA comment field of the database. Affected samples are summarized in Table A-4.

CDM qualified as estimated (G,UG) any data associated with samples that had TCMX recoveries outside of a range of 60%-150%. For SDG 170825, five field samples and the matrix spike/matrix spike duplicate sample associated with one of the five samples had no recovery of TCMX; two field samples in SDG 172776 had no TCMX recoveries and one sample in SDG 172132 had a TCMX recovery below 10%. CDM properly rejected (R) the results for these eight field samples. These results were considered to be not usable.

- **Matrix Spike/Matrix Spike Duplicate Recoveries**

Within each SDG, two aliquots of a representative sediment sample were spiked with a suite of 20 congeners (BZ#8, 18, 28, 44, 52, 66, 77, 101, 105, 118, 126, 128, 138, 153, 170, 180, 187, 195, 206, and 209). The purpose of the spikes was, in part, to evaluate the accuracy of the analytical method relative to laboratory performance and specific sample matrix. The advisory limits for spiked congener recoveries are 60%-150%. TAMS/Gradient noted no significant spike recovery problems for any of the high resolution sediment cores. Matrix spike/matrix spike duplicate analyses were analyzed for 30 high resolution sediment core samples. This represents a frequency of 6.1%, which exceeds the 5% requirement stipulated in Phase 2A SAP/QAPP.

- **Congener Identification**

TAMS/Gradient established qualitative criteria to minimize erroneous identification of congeners. An erroneous identification can be either a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). The calculated concentrations for congeners detected in both columns should not differ by more than 25% between columns (%D ≤ 25%). This criterion applies to only those congeners which can be resolved as individual congeners on both columns. If the %D for the results between the two columns is > 25% but ≤ 50% the results were estimated. If the %D was > 50% but ≤ 90%, the results were estimated and presumptively present (GN). If the %D between columns was > 90%, the results were unusable (R).

TAMS/Gradient noted extensive problems with congener identifications as a result of dual column imprecision for numerous SDGs, including 166783, 172897, 171177, 172592, 170805, 172624, and 169787. In fact, the majority of the estimated and rejected data for the high resolution sediment coring study was a result of dual GC column imprecision. Of particular note was SDG 169787, for which 78 congener results were rejected, including BZ#18 (a principal congener) for one sample. The greatest impact to the high resolution sediment coring study was to BZ#19, a principal congener, which was rejected for 78 samples. With the level of background organic material present in Hudson sediments, resultant interferences, particularly for congeners with low concentrations, likely caused these differences between the dual GC column results.

A.5.3.2 Precision

- **Matrix Spike/Matrix Spike Duplicate Comparison**

The analysis of matrix spike (MS) and matrix spike duplicate (MSD) samples can also provide valuable information regarding method precision relative to laboratory performance and specific sample matrix. The advisory limit for relative percent difference (RPD) of spiked congeners in a MS/MSD pair is 40%, and for nonspiked congeners, the precision criterion is 40% Relative Standard Deviation (RSD).

TAMS/Gradient noted MS/MSD precision exceedances for only 4 SDGs (170825, 168494, 172897, and 172148). Regarding principal congeners, BZ#28 had a 57% RPD for SDG 168494 and the %RPD ranged from 43% to 63% for BZ#8, 18, 28, and 52 for SDG 172148. Overall, MS/MSD performance for the high resolution sediment coring study was good.

A.5.3.3 Representativeness

- **Field Duplicate Results**

Analysis of field duplicate samples provides an indication of the overall precision of the sampling and analysis program. These analyses measure both field and laboratory precision; therefore, the results will likely have more variability than laboratory duplicates and MS/MSD samples, which only measure laboratory precision. Data validators used a 50% RPD criteria for evaluating field duplicate precision. Any congener precision greater than 50% RPD was qualified as estimated (G).

A total of 28 field duplicate samples were analyzed for the high resolution sediment coring study. This represents a frequency of 5.7%, which exceeds the 5% requirement stipulated in the Phase 2A SAP/QAPP. Overall, field duplicate precision was acceptable; especially in the context of river sediments, which are typically heterogeneous. Typically a few congeners were qualified for each pair of co-located sediments. Four SDGs had significant numbers of congeners with RPDs

greater than 50%. These include SDG 172592 (26 congeners greater than 50%), 170825 (29 congeners greater than 50%), 167188 (35 congeners greater than 50%), and 170473 (42 congeners greater than 50%). Table A-5 summarizes the duplicate precision results for the 12 principal congeners for each field co-located sample. Only one SDG (172592-Core 23) had serious precision problems for the principal congeners, and to a lesser extent SDG 170825-Core 18. TAMS/Gradient scrutinized the data in SDG 172592 for errors, but found none. Based on the difference in percent moisture between the two co-located samples (70% *versus* 47.8%), the differences are suspected to be a result of extreme sample heterogeneity.

A.5.3.4 Sensitivity

- **Blanks**

An important data quality objective associated with the high resolution sediment coring study was to obtain detection limits as low as the analytical method could produce. One effect of this approach is to register low level blank contamination during the preparation and analysis of the sediments. As such, numerous congeners in all samples in all SDGs required blank contamination qualifications. TAMS/Gradient reviewed the distribution of blank contaminants and found most contamination associated with the monochlorobiphenyls, particularly with BZ#2. Blank levels for BZ#2 usually ranged from 20 ppb to 80 ppb in extract, with a maximum of 209 ppb in extract for SDG 169011. Since BZ#2 is not a dechlorination product, a major Aroclor component, or a principal congener, TAMS/Gradient did not consider this to be a serious data quality problem. BZ#1, a principal congener, was usually significantly lower in concentration in blanks than was BZ#2; but was present in an enormous concentration (308 ppb in extract) for SDG 166308. BZ#4, a principal congener, was often present in blanks from 10 ppb to 20 ppb in extract for most SDGs.

CDM qualified results during data validations with a "B", which indicated that the result was within 5 times of the blank action level. TAMS/Gradient converted all "B" qualified results in the database to nondetect results due to uncertainty in this detection. Table A-6 summarizes the congener detects changed to non-detects.

- **Quantitation Limits**

Evaluating dechlorination processes and modeling transport pathways of PCB congeners in sediments necessitated obtaining low detection limits. TAMS/Gradient and Aquatec devised analytical methods to enhance lower detection limits. This, in part, required employing sample/extract cleanup methods to remove matrix interferences, and maximizing sample size when possible. For the high resolution coring study, TAMS/Gradient defined optimum detection limits as 1 µg/kg for monochlorobiphenyls, 0.5 µg/kg for dichlorobiphenyls through hexachlorobiphenyls, and 0.5-1 µg/kg for heptachlorobiphenyls through decachlorobiphenyl. Results of the MDL study necessitated raising the detection limit for BZ#2 (a monochlorobiphenyl) significantly above these requirements (approximately a factor of 3).

In general, achieving appropriate detection limits for the sediment samples was not a problem. Whenever TAMS/Gradient noted raised detection limits, the affected samples contained high organic content; specifically the presence of PCBs. The relative ratio of congeners detected within each high-concentration sample remained reasonably consistent, therefore the elevated detection limit for nondetected congeners did not affect data usability. Aquatec achieved adequate detection limits for critical low level samples used for delineating the outer boundaries of sediment contamination, or other PCB sources (*e.g.*, tributaries).

A.5.4 Usability - Principal Congeners

The 12 principal target congeners employed in the high resolution sediment coring study are key to delineating PCB geochemistry in the Hudson River. The following synopsis will provide data users with the strengths and weaknesses of the principal target congener data within the context of this study:

BZ#1. The reported results for BZ#1 met the data quality objectives of the program. Results for 14 sediment samples were rejected (out of 495 samples) due to dual GC column imprecision. Analytically, BZ#1 eluted as a single peak on one GC column and coeluted on the other GC column, which was acceptable for the purposes of this program. Regarding sensitivity, for SDG 169803 no response was obtained for BZ#1 on the SB-octyl 50 column

during the entire analytical sequence, hence all BZ#1 data for this SDG was considered presumptively present. This data is usable as a result of the documentation of its historical presence in Hudson River sediments. With regard to detection limits, monochlorobiphenyls were initially optimized to 1 ppb. In fact, detection limits for BZ#1, a monochlorobiphenyl, were generally realized to be 1 to 6 ppb, which were acceptable, with one notable exception for SDG 166308. The blank contamination for this SDG was 308 ppb in extract, which resulted in significantly higher detection limits for all samples.

BZ#4. The reported results for BZ#4 met the data quality objectives of the program. Results for 11 sediment samples were rejected due to dual GC column imprecision. Analytically, BZ#4 eluted as a single peak on one GC column, and coeluted with BZ#10, another principal congener, on the other GC column. Data for both BZ#4 and BZ#10 were considered usable. With regard to detection limits, a goal of 0.5 ppb was established. In general, this goal was met, however, there were many samples with associated blank levels of 10 ppb to 20 ppb in extracts of BZ#4, which required raising the detection limit. This did not affect data usability.

BZ#8. The reported results for BZ#8 met the data quality objective of the program. Results for nine sediments samples were rejected due to dual GC column imprecision. Analytically, BZ#8 eluted as a single peak on one GC column and coeluted with BZ#5 on the other GC column, which was acceptable for the purposes of this program. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike results for BZ#8 further indicated that the method was successful.

BZ#10. The usability assessment for BZ#10 is similar to that for BZ#4. BZ#10 eluted as a single peak on one GC column and coeluted with BZ#4 on the other GC column. Data for both BZ#4 and BZ#10 were considered usable. Results for 6 sediment samples were rejected due to dual column imprecision. In general, the detection limit goal of 0.5 ppb was met.

BZ#18. Numerous results for BZ#18 were initially rejected by the data validator due to poor dual column precision. The TAMS/Gradient Program QAO changed the rejection qualifier to a presumptively present qualifier based on the presence of BZ#18 in historical sediment

samples containing PCBs, the consistent PCB congener pattern distribution present throughout the Hudson River sediment, and GC/ITD confirmational analysis on about 10% of the data. However, 12 sediment samples still remained rejected due to dual column imprecision. Analytically, BZ#18 eluted as a single peak on one GC column and coeluted on the other GC column. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike results for BZ#8 further indicated that the method was successful. As such, the reported results for BZ#18 met the data quality objectives of the program.

BZ#19. Results for 78 sediment samples were rejected due to dual GC column imprecision. The results rendered 16% of all BZ#19 data unusable. This loss of data did not affect the overall integrity of the program. The reported results for BZ#19 met the data quality objectives of the program. Analytically, BZ#19 eluted as a single congener on both GC columns. The detection limit goal of 0.5 ppb was met for nearly all samples.

BZ#28. The reported results for BZ#28 met the data quality objectives of the program. Results for seven sediment samples were rejected due to dual GC column imprecision. Analytically, BZ#28 eluted as a single congener peak on both GC columns. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike results for BZ#28 further indicates the method was successful.

BZ#52. The reported results for BZ#52 met the data quality objectives of the program. Results for two sediment samples were rejected due to dual GC column imprecision. Analytically, BZ#52 eluted as a single congener peak on both GC columns. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike recovery for BZ#52 further indicated that the method was successful.

BZ#101. Data users should be aware that BZ#101 always coeluted with BZ#90 (on both GC columns), and therefore was always reported with BZ#90. For reported results, all other QA/QC requirements were met, therefore should be considered usable. No sample results were rejected. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike results for BZ#101 further indicated that the method was successful.

BZ#118. The reported results for BZ#118 met the data quality objectives of the program. Results for 12 sediment samples were rejected due to dual column imprecision. Analytically, BZ#118 eluted as a single peak on both GC columns. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike results for BZ#118 further indicated that the method was successful.

BZ#138. The reported results for BZ#138 met the data quality objectives of the program. Results for three sediment samples were rejected due to dual column imprecision. Analytically, BZ#138 eluted as a single peak on one GC column and coeluted on the other GC column. The detection limit goal of 0.5 ppb was met for nearly all samples. Matrix spike results for BZ#138 further indicated that the method was successful.

BZ#180. The reported results for BZ#180 met the data quality objectives of the program. Results for three sediment samples were rejected due to dual column imprecision. Analytically, BZ#180 eluted as a single peak on one GC column and coeluted on the other GC column. The detection limit goal of 0.5 ppb to 1 ppb was met for nearly all samples. Matrix spike results for BZ#180 further indicated that the method was successful.

A.5 Conclusions

The PCB congener analytical chemistry program implemented by TAMS/Gradient for the Hudson River high resolution sediment coring study required the development and use of program-specific GC/ECD methodology in order to generate data meeting the data quality objectives of the program. A total of 495 sediment samples were analyzed for 126 target and non-target congeners. Considering the complexity of the program, TAMS/Gradient considers the outcome of the analytical chemistry program to have been successful.

A summary of the number of qualifiers applied to each PCB congener is tabulated in Table A-7. For the high resolution sediment coring study, 62,426 congener measurements were recorded, of which 1,918 values were rejected. Congeners most often rejected include BZ#2 (19%), BZ#3 (26%), BZ#19 - a principal congener (16%), BZ#40 (11%), BZ#41 (11%), BZ#126 (14%), BZ#190

(11%), and BZ#193 (10%). The reason for most of these rejections was the imprecision between the GC columns. A 96.9% completeness rate was achieved for this program, which successfully exceeded the 95% completeness goal. The only principal congener that did not meet the completeness goal was BZ#19 (84% completeness), however, this did not impair the overall integrity of the program.

A majority (67.1%) of all congener data (both detects and nondetects) were qualified. Again, the main reason for most of the qualifications was the result of exceedances in the dual GC column precision criteria. Numerous congeners for nearly all SDGs had calculated concentrations on each GC column which differed by more than 25%, but less than 50%, which warranted qualification as estimated values. With the level of background organic material present in Hudson sediments, resultant interferences, particularly for congeners with low concentrations, likely caused these differences between the GC columns. Other problems contributing to data qualification included missed holding times, sporadic problems with TCMX surrogate recoveries, and some GC/ECD calibration problems. Data users should consider all detected and nondetected results which were estimated to be usable relative to the data quality objectives of the program.

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APPENDIX B

DATA USABILITY REPORT FOR PCB CONGENERS WATER-COLUMN MONITORING PROGRAM

B.1 INTRODUCTION

The usability of data relates directly to the data quality objectives of the environmental investigation (Maney and Wait, 1991; USEPA, 1993, 1994). The Hudson River PCB congener chemistry program required sophisticated, high resolution gas chromatography analyses with stringent quality control criteria. In addition, various inorganic and physical parameters were analyzed to define the chemical context within which the PCB congeners exist. This approach was necessary to delineate the concentration of PCB congeners within the context of geochemical and biological processes occurring in the river.

Initially, TAMS/Gradient selected 90 PCB congeners as target congeners based on their significance in environmental samples and the availability of calibration standards. In addition, qualitative and quantitative information for an additional 36 PCB congeners (non-target congeners) was obtained from each water sample analysis using relative retention time information detailed in the literature, and more recently verified with actual standards. In addition to these 126 PCB congeners, for certain sampling episodes (Transect 6 and flow-averaged events 4, 5, and 6) Aquatec analyzed an additional 17 PCB congeners.

Certain target congeners are of particular importance in evaluating geochemical and biological processes within the Hudson River water-column. These are the 12 "principal" target congeners, which consist of BZ# 1, 4, 8, 10, 18, 19, 28, 52, 101, 118, 138, and 180. The focus of this report will be on the usability of the analytical data for these principal congeners. However, the importance of accurately measuring all individual congeners is greater for the water-column samples than the high resolution sediment coring samples because all individual congeners were employed to determine congener-specific water/particulate partition coefficients.

This report serves as an overall evaluation of the PCB congener analyses performed for the Hudson River water-column monitoring program. The evaluation is based on the assessment of data quality relative to the objectives of the study. The report will first provide a synopsis and assessment of the field sampling, analytical chemistry and data validation programs, and then evaluate data usability for all the 126 congeners with particular emphasis on the principal target congeners. A data usability report assessing the non-PCB chemical and physical analyses for the water column samples is provided in Appendix C.

B.2 FIELD SAMPLING PROGRAM

TAMS/Gradient designed the water-column monitoring program to investigate water-column PCB levels, transport, sources, and dissolved phase to suspended matter partitioning of PCB congeners. This was accomplished by sequential sampling along transects for whole water, filtered water and particulates (water-column transect study); and collecting flow-averaged composite samples (flow-averaged water-column sampling study) to provide a measure of mean total PCB transport in the Upper Hudson from Baker Falls to Waterford. The flow-averaged water-column sampling study provides a perspective on river conditions midway between the instantaneous conditions determined by the water-column transect study and the long-term average water-column conditions determined by the high resolution sediment coring program. The water-column monitoring collection program, sampling procedures, analytical protocols, and quality control/quality assurance requirements are described in the "Phase 2A Sampling and Analysis Plan/Quality Assurance Project Plan - Hudson River PCB Reassessment RI/FS" (TAMS/Gradient, May 1992, referred to in this report as the Phase 2A SAP/QAPP). A summary of the subsampling and analysis scheme is provided in Figure B-1.

The water-column transect study consisted of six sampling events (transects) occurring approximately monthly at 13 stations in the Upper Hudson River and spanning the high-flow spring-runoff event. In addition, monitoring at four stations in the Lower Hudson coincided with three Upper Hudson events. The timing of sampling at sequential stations in the Upper Hudson was designed to monitor the same parcel of water moving downstream. One exception to this scheme was Transect 8, which occurred on April 23, 1993. Samples were not sequentially collected during

this transect. Instead, sample collection at this transect was conducted near the annual peak flow. A subset of samples from the transect program representative of the main-stem Hudson River (not tributaries or sources) were used for an equilibration study. Samples from Saratoga Springs were used for blanks. The study consisted of samples being stored for four days, with occasional stirring, prior to being submitted to the analytical laboratory for analysis.

The flow-averaged water-column sampling study consisted of a series of six 15-day sampling events conducted over a period of six months overlapping the water-column transect study. Sampling occurred at four Upper Hudson stations coinciding with water-column transect stations, and involved compositing of samples collected every other day at each station over a 15-day period. This resulted in eight individual samples per a 15-day period. For flow-average event 7, four separate temporal composites were collected from Waterford. These samples were collected daily over a two to four week period and then composited into one sample.

TAMS/Gradient initiated sampling for the water-column monitoring program on January 29, 1993 and concluded on September 23, 1993. Scientists from TAMS and Rensselaer Polytechnic Institute (RPI) performed the sampling. The sampling team collected a total of 135 pairs of filtered water and particulate samples (on filters). Aquatec allocated these samples into 14 Sample Delivery Groups (SDGs). In addition, the sampling team collected 14 whole water (*i.e.*, unfiltered) samples. The TAMS/Gradient Program Quality Assurance Officer (QAO) conducted a field sampling audit on March 26, 1993 to assess compliance of the sampling procedures with the Phase 2A SAP/QAPP. The audit findings indicate that the sampling program was being conducted in a technically acceptable manner consistent with the Phase 2A SAP/QAPP (Wait, 1993b).

B.3 ANALYTICAL CHEMISTRY PROGRAM

B.3.1 Laboratory Selection and Oversight

TAMS/Gradient retained a number of analytical laboratories to perform the analyses required for this program. To verify that the selected laboratories had the capacity, capabilities, and expertise to perform sample analyses in strict accordance with the specified methodologies; each qualifying

laboratory underwent an extensive audit by TAMS/Gradient's senior chemists. TAMS/Gradient retained the following two laboratories to perform water-column sample analyses for the Hudson River RI/FS program: Aquatec Laboratories, a division of Inchcape Testing Service located in Colchester, Vermont; and Rensselaer Polytechnic Institute located in Troy, New York. A USEPA Special Analytical Services (SAS) contract laboratory, Chemtec Consulting Group Inc., located in Englewood, New Jersey, was also retained through the SAS procurement process. Aquatec was the sole analytical laboratory which conducted the PCB congener analyses for the entire program.

TAMS/Gradient conducted routine laboratory audits of RPI and Aquatec during the water-column monitoring program to verify compliance of each laboratory with the Phase 2A SAP/QAPP requirements. TAMS/Gradient did not perform audits of the USEPA SAS laboratories.

Unique requirements of the PCB congener method necessitated refinements of previously published methods. In conjunction with these changes, Aquatec conducted Method Detection Limit (MDL) studies and Extraction Efficiency (EE) studies for river water to verify the adequacy of the methods. The TAMS/Gradient Program Quality Assurance Officer oversaw and approved the method refinements throughout the program.

B.3.2 Analytical Protocols for PCB Congeners

The method used by TAMS/Gradient for the determination of PCB congeners in Phase 2A is a program-specific method based on NYSDEC's Analytical Services Protocol Method 91-11 (NYSDEC, 1989) for PCB congeners. Appendix A4 of the Phase 2A SAP/QAPP describes procedures for the calibration, analysis, and quantitation of PCB congeners by fused silica capillary column gas chromatography with electron capture detection (GC/ECD). The method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. Aquatec extracted water and filter samples with hexane, and performed applicable cleanup procedures prior to analysis by GC/ECD, as detailed in Appendix A3 of the Phase 2A SAP/QAPP. Aquatec analyzed hexane extracts for PCB congeners on a dual capillary-column GC/ECD, as detailed in Appendix A4 of the Phase 2A SAP/QAPP. Aquatec identified PCB congeners using comparative retention times on two independent capillary columns of different polarity. Aquatec used calibration standards for each congener to define retention times. In addition, Aquatec routinely analyzed Aroclor standards and

mixtures of Aroclor standards to verify identification and quantification of the primary calibration standards. Due to the non-linear nature of the ECD over any significant calibration range (for this project 1 to 100 ppb in extract), Aquatec generated the calibration curves used for quantitation from a quadratic weighted least squares regression model where the correlation coefficient is greater than 0.99 (McCarty, 1995; EPA, 1986 - Method 8000B, proposed 1995 update). For each PCB congener which elutes as a single congener on each GC column, Aquatec reported the result as the lower of the two values. Although this quantitation scheme is compliant with USEPA CLP guidelines for dual-column analyses (USEPA, 1991), it may introduce a slight low bias when calculating homologue and total PCB sums. TAMS/Gradient compared data in the database relative to absolute results on both columns and found the bias was usually negligible, and on a worse-case basis, may be 2% to 10% low. For situations where coelution occurred on one column, Aquatec quantitated the result from the column not displaying coelution. If only coelution results were available, Aquatec performed a calculation to decipher concentrations using response factors derived by Mullen (1984). For the 12 principal congeners, BZ#19, 28, 52, and 118 eluted as a single congener peak on both GC columns. BZ#1, 4, 8, 10, 18, 138, and 180 eluted as a single congener peak on one column and coeluted on the other column. BZ#101 coeluted on both columns and was always reported with BZ#90.

Approximately 10% of all samples analyzed by GC/ECD also underwent additional analysis using a GC-ion trap detector (ITD) as an additional means of confirming PCB congener identifications, as detailed in Appendix 5A of the Phase 2A SAP/QAPP. Where possible, Aquatec selected samples with the highest concentrations of PCB congeners for confirmation analysis by GC/ITD. Aquatec usually performed two GC/ITD analyses per SDG, even if congener concentrations were minimal throughout the SDG.

MDL and EE studies were conducted in accordance with USEPA (1984) guidance to ensure that the methods adequately addressed the program data quality objectives. For the water-column samples, this included studies for nominally 16-liter filtered water samples and the associated suspended matter filters (particulates), and 1-liter whole (unfiltered) water collected from the Hudson River. With regard to the MDL studies, acceptable results were found for the 16-liter filtered water samples and suspended matter filters. For the 1-liter whole water samples, some congener detection limits were significantly higher than the objectives specified in the Phase 2A SAP/QAPP, especially for the monochlorobiphenyls. No acceptable technical alternatives were available; therefore, the

elevated detection limits were adopted for the program. For this reason, 1-liter samples were collected and analyzed for only Transect 1. PCB congeners were not present in high enough concentrations to provide meaningful results on the first set of Hudson River water samples for the EE study. Therefore, the study was reconducted with new river water samples containing higher concentrations of PCBs and found to be acceptable. A synopsis of the MDL/EE studies is provided in a TAMS/Gradient memorandum dated July 1, 1993 (Cook, 1993). At the start of the Phase 2A sampling and analysis program, TAMS/Gradient and Aquatec selected 90 target PCB congeners. These target congeners are listed in Table A-1 and identified by BZ number (Ballschmiter and Zell, 1980). TAMS/Gradient and Aquatec based the selection of these 90 PCB congeners on their significance in environmental samples and the commercial availability of calibration standards. TAMS/Gradient referred to PCB congeners for which calibration standards were available as "target congeners". To verify that congener response for these calibration standards was reproducible over time, TAMS/Gradient examined calibration data from November 1992 and October 1993. TAMS/Gradient found temporal consistency to be acceptable on both GC columns (Bonvell, 1994a).

The high resolution column chromatography techniques employed by Aquatec produced acceptable PCB resolution for numerous congeners not contained in the target congener calibration standards. Thus, TAMS/Gradient decided during method refinement to report approximately 50 additional PCB congeners. The laboratory identified these additional PCB congeners based upon the relative retention times reported in the published literature (Mullen, 1984; Schulz, 1989; Fischer and Ballschmiter, 1988, 1989). Aquatec calibrated these additional "non-target" congeners using the calibration curve for target congener BZ#52. Aquatec chose BZ#52 because it elutes as a single congener peak in the middle region of the chromatogram for both GC columns and is a major component of Aroclor 1242, the Aroclor anticipated in Hudson River samples. Using additional congener calibration standards which became commercially available by August 1993, Aquatec performed analyses to verify and refine the historical relative retention times, and to determine individual congener calibration parameters. These analyses confirmed a majority (36) of the historical non-target congener relative retention times. For all analyses performed prior to August 1993, the results for 14 non-target compounds not confirmed by this analysis TAMS/Gradient considered unusable and deleted from the database. A review of project data indicated that the 36 confirmed non-target congeners represent a significant percentage, up to 25%, of the total PCB mass. Therefore, TAMS/Gradient decided to include the non-target congener results to calculate homologue and total

PCB masses in the Hudson River. Omission of these non-target congener results would have resulted in a significant low bias in the resulting calculations for homologue and total PCBs. Thus, 36 non-target congeners are included in this report, as shown in Table A-1. Since the non-target congener results were to be included in the calculations of homologue and total PCB mass, TAMS/Gradient applied an individual correction factor to each congener's results based on the analysis of the additional congener standards. The application of these correction factors served to minimize the uncertainty associated with quantitation of non-target congeners. A series of TAMS/Gradient memoranda describe the method for deriving these calibration correction factors (Bonvell, 1993a,b,c). A listing of the derived calibration correction factors is provided in a TAMS/Gradient memorandum (Bonvell, 1994b).

To establish a method of quantitating total Aroclor concentrations from PCB congener data, Aquatec performed duplicate analyses of seven Aroclor standards (1016, 1221, 1232, 1242, 1248, 1254, 1260). TAMS/Gradient defined the quantitation of an Aroclor for this program as the sum of all congeners present in the standard Aroclor mixture at a concentration greater than 0.1% of the total Aroclor mass. In this manner, TAMS/Gradient then compared the percentage of the total mass represented by the detected target and non-target congeners greater than 0.1% of the Aroclor mass to the actual concentrations of each Aroclor standard. The results produced the following mass yields for the seven Aroclor standards: Aroclor 1016=93.3%, Aroclor 1221=86.6%, Aroclor 1232=91.0%, Aroclor 1242=90.6%, Aroclor 1248=89.2%, Aroclor 1254=95.8%, and Aroclor 1260=87.0%. Thus, in each case, the 90 target and 36 non-target congeners represented more than 87% of the original Aroclor mass. For those Aroclors most important to the Hudson River based on General Electric's reported usage (Brown *et al.*, 1984), these congeners represented better than 90% of the Aroclor mass (*i.e.*, Aroclors 1242, 1254, and 1016). A further discussion of the results of the Aroclor standards analyses is presented in Section 4.3 of the main body of the report.

As a part of the TAMS/Gradient monitoring of Aquatec's method performance, a blind spiked water sample (*i.e.*, performance evaluation [PE] sample) was supplied to the laboratory (Sample TW-003-0020, SDG 181370). For the most part, the PE results were reasonable (Wait, 1993b). TAMS/Gradient noted no significant false positives. Recoveries were fairly consistent, but rather low, ranging from 62 to 76%. These values are all within the acceptable range for matrix spike sample recoveries (60%-150%). However, for most congeners these values are typically lower than what was experienced in the actual water column sample analyses (generally greater than 90% recovery). This

difference may be due to losses in the field during preparation of the sample (*e.g.*, spilling, weighing and dilution). One significant false negative was discovered (*i.e.*, laboratory failure to report a detection of BZ#187), which required a reevaluation of one of the GC columns used for analysis. This situation is discussed in more detail in the data usability section of this report.

B.4 DATA VALIDATION

An essential aspect of understanding the uncertainties of the Phase 2 water-column data is understanding the significance of the qualifiers associated with the results. Each result has an associated qualifier. Qualifiers denote certain limitations or conditions that apply to the associated result. Initially, the analytical laboratories applied qualifiers to the results, and then the data validators modified the qualifiers, as necessary, based on the established validation protocols. Data reporting and validation qualifiers direct the data users concerning the use of each analytical result. TAMS/Gradient used two sets of qualifiers in the database, one set for PCB congener data, and a second set for non-PCB chemical and physical data. Aquatec developed an extensive list of data reporting qualifiers to be applied to the PCB congener data. The list is based on standard USEPA qualifiers used for organic analyses, with additional qualifiers provided to note unique issues concerning PCB congener analysis, *e.g.*, the quantitation scheme. The data reporting qualifiers for PCB congener data, as applied by Aquatec, are defined in detail in Table A-2 of Appendix A. Qualifiers for non-PCB data are discussed in Appendix C.

During validation, the validators made modifications to the data qualifiers which are reflected in the database. CDM Federal Programs Corporation and their subcontractors, under a separate USEPA contract, performed data validation for the water-column monitoring program. Validation procedures employed by CDM for GC/ECD analyses are detailed in Appendix A6 of the Phase 2A SAP/QAPP, and validation guidelines for GC/ITD analyses are provided in Appendix A7 of the Phase 2A SAP/QAPP. TAMS/Gradient devised the validation procedures to reflect the data quality objectives of the program, as well as to conform with USEPA (1988, 1992a) standards as appropriate. USEPA Region II concurred with these method-specific validation protocols. In addition, TAMS/Gradient designed comprehensive data validation templates to facilitate consistency of approach and actions during validation. Prior to validation of the PCB data, Gradient conducted a training

workshop to aid CDM in properly performing the validation. Gradient reviewed and commented on the initial CDM validation reports and provided real-time QA oversight. All validation reports were inspected by the Program QAO, with only minor errors readily apparent. USEPA Region II (Lockheed ESAT) revalidated data for 16 water-column samples. Lockheed ESAT noted no significant problems.

The initial data validation efforts for the high resolution sediment core samples and water column samples were completed in December 1994. The results were subsequently incorporated into the TAMS/Gradient database and available for review in March 1995. However, by April 1995, it became clear that the validation results differed markedly but randomly from the unvalidated data. Upon further investigation, the project staff at TAMS identified the source of some of these differences as the result of incorrect data validation procedures largely pertaining to blank corrections. Specifically, it was found that blank samples were sometimes incorrectly associated with environmental samples and blank values were transcribed incorrectly among validation records, among other concerns. These problems were found to be extensive enough that USEPA, in agreement with TAMS/Gradient, decided to have both the entire high resolution sediment coring and the water-column monitoring PCB analysis data validation program redone to minimize manual data manipulation and transcription (*e.g.*, Garvey, 1995). TAMS developed a computer spreadsheet macro for data validation in July 1995. This macro electronically applied blank qualification criteria (*i.e.*, the "B" qualifier) to the electronic data files using an algorithm developed from the data validation procedures. These files were then used to generate the standard data validation forms incorporated in the validation packages. Subsequent to the electronic validation, CDM reviewed all data for blank qualifier assignment before approving the data validation packages. As a result of this review, minor changes in the macro had to be made to handle unusual data packages (*e.g.*, extra congeners reported). Using the data validation macro, CDM completed the revalidation of the high resolution sediment coring and water column PCB samples in September 1995.

As an overall assessment of data quality, the TAMS/Gradient Program QAO reviewed pertinent aspects of the sampling and analysis program (*e.g.*, historical data, implementation of sampling protocols, laboratory performance) relative to the data quality objectives. Decisions on data usability sometimes overrode data qualification codes, as justified in this report. All qualifier changes made by the TAMS/Gradient Program QAO, as reflected in this data usability report, are noted in the final database (code Y in QA Comment field of database). For the water-column monitoring program, the TAMS/Gradient Program QAO modified 115 qualifiers out of 20,448 PCB congener data records as

a result of data usability issues, representing 0.56% of the data. The only qualifier change involved unrejecting results for three samples (TS0040017, F2-001-0000[TS], and TS-001-0009) associated with poor octachloronaphthalene (OCN) surrogate recoveries.

B.5 DATA USABILITY

B.5.1 Approach

Most previous studies of PCB chemistry in Hudson River waters have focused on the concentration of specific Aroclors, total PCBs and/or the distribution of PCB homologues. The current assessment of PCB fate and distribution in the Hudson River required TAMS/Gradient scientists to implement sophisticated equilibrium chemistry and transport modeling studies requiring concentration ratios of certain PCB congeners. Of the 90 target and 36 non-target congeners, 12 target congeners are of particular importance. The usability of these "principal" congeners is key to the water-column monitoring program.

Principal congeners will be employed in the following studies by the data users:

Molar dechlorination product ratio - The molar sum of BZ#1, 4, 8, 10, and 19 are compared to the molar sum of all 126 congeners analyzed. This ratio is then compared to a similar index for Aroclor 1242 to assess, calculate, and evaluate the extent of dechlorination.

Transport modeling - BZ#4, 28, 52, 101, and 138 are considered independently as compounds modeling PCB transport.

Aroclor 1016 and 1242 - BZ#18 is used to estimate the potential contribution of Aroclor 1016 and 1242 to Hudson River waters.

Aroclor 1254 - BZ#118 is used to estimate the potential contribution of Aroclor 1254 to Hudson River waters.

Aroclor 1260 - BZ#180 is used to estimate the potential contribution of Aroclor 1260 to Hudson River waters.

Thus, 12 principal congeners (BZ#1, 4, 8, 10, 18, 19, 28, 52, 101, 118, 138, and 180) are the focus of this usability report. However, the remaining target and non-target congeners have important implications to the water-column monitoring program. TAMS/Gradient used these congeners to calculate the concentrations of total PCBs, PCB homologues, and Aroclor mixtures. Homologue group information was more relevant for the water-column monitoring program than for the high resolution sediment coring study. In addition, partition coefficients have been calculated for each congener for the purpose of trend analysis. Each of the 126 congeners is employed to evaluate partition coefficients. In this regard, the accuracy of the individual congener concentrations in the water-column monitoring program is more important than in the high resolution sediment coring study.

B.5.2 Usability - General Issues

The data quality objectives for the Hudson River water-column monitoring program required that the development of a sensitive program-specific gas chromatography method. Available standard agency methods were not adequate to achieve the congener-specific identifications and detection limits needed for the project. TAMS/Gradient based the method utilized on a modified NYSDEC ASP Method 91-11 (1989) protocol encompassing information published in the literature, as well as in-house research conducted by Aquatec. This research included conducting Method Detection Limit (MDL) studies and Extraction Efficiency (EE) studies in accordance with USEPA (1984, 1986) guidance. During the course of these studies, and the inception of the water-column monitoring program, TAMS/Gradient and Aquatec noted various nuances to the methods that required refinement. As such, TAMS/Gradient and Aquatec made modifications to some of the original protocols. The remainder of this section discusses some of the more significant changes and their ramifications.

Identification of Non-Target Congeners

At the beginning of this program, Aquatec identified non-target congeners based on historical relative retention times reported in the literature. In August 1993, Aquatec analyzed calibration standards for each of the non-target congeners. Using these additional calibration standards, Aquatec performed analyses to confirm historical relative retention times. Though these analyses verified a majority of the historical non-target congener relative retention times, some of the historical relative

retention times used to identify non-target congeners did not match the relative retention times determined by the analyses of the non-target congener standards. TAMS/Gradient deleted fourteen non-target congeners from the database for all analyses performed prior to August 1993 due to these unconfirmed identifications. The 14 non-target congeners deleted were: BZ#35, 39, 46, 100, 104, 130, 131, 132, 134, 162, 165, 173, 176, and 179. Aquatec identified and confirmed these 14 congeners based on the current laboratory-derived relative retention times for samples analyzed during and after August 1993. Therefore, the results for these 14 non-target congeners will remain in the database for all samples analyzed during and after August 1993. Use of these non-target congener data should be limited since they are not consistently available for all data sets. If a situation arises where information for the deleted non-target congeners is critical to a data user, an in-depth review of the chromatograms and re-calculation of the concentrations could potentially produce usable results for some of these congeners.

Quantitation of Non-Target Congeners

The laboratory originally quantitated non-target congeners using the calibration curve determined for BZ#52. Since the non-target congener results were to be included in the calculations of homologue and total PCB mass, TAMS/Gradient desired a more accurate method of quantifying the non-target congeners. Aquatec analyzed calibration standards for the non-target congeners in September 1993, and again in April 1994, for the determination of congener-specific response factors. Based on this information, TAMS/Gradient calculated correction factors for each non-target congener and applied these to the laboratory data within the database (Bonvell, 1994b).

Re-calculation of Some PCB Congener Results

From August 1992 to July 1993, Aquatec observed that the relative retention times of congener compounds were changing on the SB-octyl-50 GC column. The shifts in relative retention times did not effect the target compound identification except for BZ#187 and 128. This specific identification problem became apparent from the results of a blind performance evaluation sample. In the case of BZ#187 and 128, their original identification on the SB-octyl-50 analytical column showed BZ#128 eluting before BZ#187. Over the course of eight months, the two congeners merged together as one peak, then became resolved again, only BZ#187 now eluted before BZ#128. When the two congeners

resolved, Aquatec assumed that each congener eluted in the same order as previously indicated, which was incorrect. To determine the effects of the shifts on the "non-target" compounds, Aquatec analyzed individual "non-target" standards. From these data, Aquatec discovered that the initial identification of non-target PCB congener compounds obtained from Ballschmiter's research was inconsistent with this study's SB-octyl-50 analytical column results. During the review of the elution order of PCB congeners on the SB-octyl-50 column, Aquatec also discovered that BZ#91 was misidentified. TAMS/Gradient and Aquatec corrected the misidentification of BZ#91 and the other affected congeners.

Aquatec finalized the proper identification of non-target PCB congeners in November 1993. In March 1994, TAMS/Gradient instructed Aquatec to review all PCB congener data analyzed from September 1992 to July 1993 to rectify possible misidentifications. These corrections also necessitated changes in the PCB congener database. All data initially entered into the database have been validated without consideration to the changes discussed herein. Due to the GC column problem, Aquatec changed some records and TAMS/Gradient flagged those records with a "K" to facilitate comparison of original and changed records. A secondary validation of the changes has not been performed. However, the identification changes made are not expected to adversely effect the overall validity of the data. Some possible problems to be aware of include the analytical status of calibration curves and check standards for BZ#91 for the entire time period, and BZ#187 and 128 from March 17, 1993 through July 1993. Another possible problem was 'B' flags. The 'B' flag was used to indicate method blank contamination. Requantitation of results has changed the 'B' qualifier status in some cases.

GC Column Change

Initially, Aquatec used a HP-5 (or RTx-5) column and a SB-octyl-50 GC column for PCB congener analyses. In November 1993, Aquatec obtained new SB-octyl-50 columns for pending analyses of Phase 2 biological samples. Each of the new SB-octyl-50 columns showed signs of column degradation resulting in severe peak retention time shifts. Due to the concern that an acceptable SB-octyl-50 column would not be obtainable, TAMS/Gradient solicited approval from USEPA Region II for a replacement column, Apiezon_L. TAMS/Gradient was concerned about data comparability for the overall program, but had no alternative. USEPA Region II concurred with the replacement of the SB-octyl-50 column with the Apiezon_L column in December 1993. The Apiezon_L column was

selected for the following reasons:

The Apiezon_L column phase is similar to the SB-octyl-50 column phase.

The Apiezon_L column provides PCB congener separations similar to the SB-octyl-50 column.

The PCB congener retention times on the Apiezon_L column are more stable than on the SB-octyl-50 column.

The NYSDEC analytical laboratory performing Hudson River PCB congener analyses was using the Apiezon_L column successfully for fish samples.

In February 1994, Aquatec performed a comparison study for the two column sets, HP-5/SB-octyl-50 and HP-5/Apiezon_L (Cook, 1994). Aquatec analyzed four Phase 2 pilot fish samples on both the HP-5/SB-octyl-50 column combination and also the RTx-5/Apiezon_L column combination. The PCB congener results compared well qualitatively and quantitatively with few exceptions. The results for BZ#15 and 37 were consistently 2 to 10 times higher on the SB-octyl-50 column pair. Data users are cautioned that the results for BZ#15 and 37 reported through March 1994 and the same congeners reported after March 1994 are not comparable due to differences in the method of quantitation.

Lower Column Concentration Bias

The USEPA CLP protocol requires that for dual column GC analyses, the lower of the two values from each column will be reported (USEPA, 1991). TAMS/Gradient incorporated this same quantitation scheme into this program. This quantitative method may introduce a slight low bias when calculating homologue and total PCB sums. TAMS/Gradient determined that this bias was usually negligible, and on a worst-case basis, may be as much as 2% to 10% low. Therefore, the data user should consider these totals as usable, but estimated values, due to the uncertainties of the individual results which are summed to form these values.

Surrogate Spike Compound

At the inception of the water-column monitoring program, TAMS/Gradient and Aquatec employed two surrogates: tetrachloro-m-xylene (TCMX) and octachloronaphthalene (OCN). Aquatec

noted soon after the program began that OCN recoveries were a problem. For many of the water-column samples, recoveries were less than 10% and sometimes 0%, although the TCMX and matrix spike/matrix spike duplicate results for these same samples were usually acceptable. Reextraction and reanalysis of the same samples produced similar results. The purpose of surrogate spike analyses is to evaluate the performance of the extraction procedure. TAMS/Gradient and Aquatec determined OCN was an inappropriate surrogate for this program. Research by Aquatec suggests that OCN was breaking down to heptachloronaphthalene and hexachloronaphthalene. During the validation process, CDM rejected data that had OCN recoveries below 10%. During this data usability assessment, the TAMS/Gradient Program QAO considered these results to be usable and changed the R qualifier to a J qualifier (estimated results) for any result solely rejected due to poor OCN recoveries.

Confirmation by GC/ITD

Aquatec analyzed approximately 10% of all samples analyzed by GC/ECD by GC/ITD to provide an additional mechanism to verify congener identification and, as a secondary objective, quantitation of congeners. The ITD is not as sensitive as the ECD (approximately an order of magnitude less sensitive); therefore, when possible, samples with the highest concentration of PCBs were selected for GC/ITD confirmation. Although this may result in a program bias for only confirming high concentration samples, the overall effect does not impair data usability.

In addition, there is the potential for some quantitative bias associated with the GC/ITD results relative to the GC/ECD results. Aquatec quantified each congener detected in the GC/ITD analysis using an average response factor per level of chlorination rather than using response factors determined specifically for each individual congener. As such, potential bias, which will vary for each congener within a chlorination homologue group, is present with the GC/ITD results. Since the ITD method was not designed to be a primary quantitative tool, some variations in quantitative results were expected. TAMS/Gradient considered quantitative differences between the GC/ITD and GC/ECD results less than a factor of five acceptable, while differences greater than five times are rejected, were considered unacceptable and associated results rejected.

B.5.3 Usability - Accuracy, Precision, Representativeness, and Sensitivity

TAMS/Gradient established a quality assurance system for this program to monitor and evaluate the accuracy, precision, representativeness, and sensitivity of the results relative to the data quality objectives. These are all important elements in evaluating data usability (*e.g.*, USEPA, 1992b, 1993). Accuracy is a measure of how a result compares to a true value. Precision indicates the reproducibility of generating a value. Representativeness is the degree to which a measurement(s) is indicative of the characteristics of a larger population. Sensitivity is the limit of detection of the analytical method.

This section will evaluate each of these parameters for the water-column monitoring program. TAMS/Gradient assessed accuracy using holding times, instrument performance and calibrations for both the GC/ECD and GC/ITD, internal standard performance for the GC/ITD, surrogate criteria for both the GC/ECD and GC/ITD, spike recoveries, matrix spike/matrix spike duplicate recoveries, compound identification results, and PE sample results (previously discussed in Section B.3). TAMS/Gradient assessed precision by comparing matrix spike, and matrix spike duplicate results. TAMS/Gradient evaluated representativeness by comparing field duplicate results, and assessed sensitivity using blank results and the sample-specific quantitation limits achieved.

Comparability and completeness are two other important data quality attributes. Comparability expresses the confidence with which data are considered to be equivalent (USEPA, 1992b). Comparable data allowed for the ability to combine the analytical results obtained from this study with previous Hudson River studies. An in-depth discussion of data comparability is provided in Chapter 3 of the main body of this report. In addition, Gauthier (1994) has provided Aroclor translation procedures for Hudson River capillary column GC data relative to previous packed column GC studies. Completeness is a measure of the amount of usable data resulting from a data collection activity (USEPA, 1992b). For this program, TAMS/Gradient established a 95% completeness goal. A discussion of completeness for the water-column monitoring program is provided in the conclusions section of this report.

B.5.3.1 Accuracy

Accuracy was evaluated based on a number of factors, including holding times; instrument performance; calibration; internal standard performance; surrogate spike recoveries; matrix

spike/matrix spike duplicate recoveries; and congener identification. These factors are discussed below:

Holding Times

Exceedance of holding times may indicate a possible loss of PCB congeners due to volatilization, chemical reactions, and/or biological alterations. Due to the persistent nature of PCBs, only severe exceedance should be considered deleterious to quantitative accuracy. For water samples and associated filters, TAMS/Gradient established an extraction holding time of 7 days from sampling, followed by an analysis holding time of 40 days from extraction.

For the water-column transect study, Aquatec extracted 11 samples (5 samples in SDG 194193 and 6 samples in SDG 179191) passed holding times by a few days. One sample in SDG 178104 missed the analysis holding time by five days. CDM qualified all affected results as estimated (G). TAMS/Gradient considered these results usable. For the flow-averaged water-column sampling study, only one SDG (183681) had any exceedances for holding times. Aquatec extracted seven water samples 11 days past holding times and one water sample extracted three days past holding time. This situation was not a result of poor performance by Aquatec, since Aquatec received the samples past holding times due to sample shipment problems. For this same SDG, the sampling team performed water filtration two weeks after sampling. All filters were extracted within holding times based on verified time of sample receipt (VTSR). CDM qualified all affected results as estimated (G). TAMS/Gradient considered these results usable.

GC/ECD Instrument Performance

Adequate chromatographic resolution and retention time stability throughout an analytical sequence are essential attributes for qualitative identification of congeners on a GC. TAMS/Gradient defined criteria for congener resolution and retention time windows in the Phase 2A SAP/QAPP. For the SB-octyl-50 column, resolution must be greater than 50% between BZ#5 and 8, 40 and 41, 183 and 185, and BZ#209 and OCN. On the HP-5 column, resolution must be greater than 25% between BZ#4,

10 and TCMX, and between BZ#31 and 28. Resolution must be greater than 50% between BZ#84 and 101/90, and between BZ#206 and OCN. Aquatec initially established retention time windows for both columns to be $\pm 0.3\%$ relative to the average initial calibration retention times for all target congeners and surrogates.

For the water-column transect study, CDM noted congener calibration standard coelution problems for BZ#5 with BZ#8 on the HP-5 column for four SDGs (#194193, 179191, 179067, and 178104). Resolution ranged from 23% to 45%. The 50% resolution criteria established by TAMS/Gradient for BZ#5/8 for this program was optimistic. Since 25% resolution was acceptable for other congeners on the HP-5 column, the TAMS/Gradient Program QAO did not consider these exceedances to be serious and they do not affect data usability. Concentrations of BZ#8 were much higher than BZ#5 in SDG 179191; therefore, CDM considered and qualified BZ#5 results presumptively present (N). CDM did not qualify BZ#8 results for SDG 179191. In addition, CDM noted coelution problems for BZ#206 and OCN on the HP-5 column for three SDGs (194193, 179191 and 179045). Aquatec did not detect BZ#206 in any samples associated with these three SDGs; therefore, no action was taken.

For the flow-averaged water-column sampling study, Aquatec encountered similar instrument performance problems. CDM noted coelution problems for BZ#5 with BZ#8, for three SDGs (190020, 194059, and 187042). In addition, BZ#206 and OCN did not resolve on the HP-5 column for SDG 194059.

GC/ITD Instrument Performance

Verifying proper GC/ITD performance required evaluating GC column resolution, ion trap detector sensitivity, and ion trap calibration. The GC resolution criteria required baseline separation of BZ#87 from BZ#154 and BZ#77. The ion trap sensitivity requires the signal/noise ratio for m/z 499 for BZ#209 and m/z 241 for chrysene-d₁₂ to be greater than 5. For ion trap calibration, the abundance of m/z 500 relative to m/z 498 for BZ#209 must be 70% but 95%. CDM noted no significant ITD performance problems for samples analyzed during the water-column monitoring program.

GC/ECD Calibration

Instrument calibration requirements were established to verify the production of acceptable quantitative data. Initial calibrations (IC) using 5-level standard concentration curves demonstrate an instrument is capable of acceptable performance prior to sample analysis. The IC criteria is 20% relative standard concentration error (% RSCE) for monochlorobiphenyl and 15% RSCE for all remaining PCB congeners and a correlation coefficient 0.995. Continuing calibration standards document maintenance of satisfactory performance over time. CDM noted some problems obtaining appropriate sensitivity for the low-level standards for BZ#2, 3, and 4. Typically, detection limits for these congeners were raised to 15 ppb in extract. Affected SDGs and congeners include 187749 (for BZ#2), 182249 (for BZ#4), 179045 (for BZ#2), 179191 (for BZ#2, 3, and 4), 179067 (for BZ#2, 3, and 4), 178104 (for BZ#2, 3, and 4), and 187042 (for BZ#2). In addition, the correlation coefficient for BZ#4 for SDG 182249 was slightly below the requirement of 0.995, thus requiring all related BZ#4 data for that SDG to be qualified as estimated (G). Finally, the % RSCE for the five point calibration curve was greater than 50% (exceeding the criteria of less than 15%) for BZ#4 for SDG 181370, thus requiring all positive results to be estimated. The TAMS/Gradient Program QAO considered the estimated results to be usable for project decisions.

GC/ITD Calibration

The initial calibration criteria for acceptable quantitative data for GC/ITD analyses required percent relative standard deviations (% RSD) of the congener relative response factor (RRF) to be less than 20%. For continuing calibration, the RRF for each congener must be within 20% of the mean calibration factor from the 5-level calibration at the beginning and end of each calibration sequence. For the water-column monitoring program, TAMS/Gradient noted no significant GC/ITD calibration problems.

GC/ITD Internal Standard Performance

To demonstrate the stability of the ITD, internal standard performance criteria were monitored. Internal standard area counts must not vary by more than 30% from the most recent calibration or by more than 50% from the initial calibration. In addition, the absolute retention time of the internal standard must be within 10 seconds of the retention time in the most recent calibration, and ion

abundance criteria must be met for chrysene-d₁₂ and phenanthrene-d₁₀. For the water-column monitoring program, TAMS/Gradient noted no significant internal standard problems.

Surrogate Spike Recoveries

Aquatec spiked surrogate compounds into all water samples prior to extraction to monitor recoveries. Recoveries may be indicative of either laboratory performance or sample matrix effects. For the water-column monitoring program, Aquatec used TCMX and OCN as surrogates. As previously discussed, OCN did not perform properly as a representative surrogate, therefore, only TCMX recoveries provide useful information for most samples. In addition to TCMX, BZ#192 was used as a surrogate for Transect 6 and Flow-Averaged Events 4, 5, and 6.

Surrogate recoveries for both the water-column transect and flow-averaged water-column sampling studies were much improved relative to the high resolution sediment coring study. Although OCN surrogate recovery performance was also better than for the high resolution sediments, OCN is still deemed an unacceptable surrogate. Therefore, three water-column transect samples which CDM qualified as rejected due to poor OCN recoveries have been unrejected to be qualified as estimated results (G or UG, as appropriate). These samples were F2-001-0000 (TS) and TS-001-0009 in SDG 178104, and TS-004-0017 in SDG 182249.

Matrix Spike/Matrix Spike Duplicate Recoveries

Within each SDG, Aquatec spiked two aliquots of a representative water sample with a suite of 20 congeners (BZ#8, 18, 28, 44, 52, 66, 77, 101, 105, 118, 126, 128, 138, 153, 170, 180, 187, 195, 206, and 209). The purpose of the spikes were, in part, to evaluate the accuracy of the analytical method relative to laboratory performance and specific sample matrix. The advisory limits for spiked congener recoveries are 60%-150%. TAMS/Gradient noted no spike recovery problems for any of the water-column monitoring samples.

Congener Identification

TAMS/Gradient established qualitative criteria to minimize erroneous identification of

congeners. An erroneous identification can be either a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). The calculated concentrations for congeners detected in both columns should not differ by more than 25% between columns (%D ≤ 25%). This criterion applies to only those congeners which can be resolved as individual congeners on both columns. If the %D for the results between the two columns is > 25% but ≤ 50%, the results were estimated. If the %D was > 50 but ≤ 90%, the results were estimated and considered presumptively present (GN). If the %D between columns was > 90%, the results were unusable (R).

TAMS/Gradient noted sporadic problems with congener identification as a result of dual column imprecision. Although the extent of the dual GC column imprecision was not as extensive as for the high resolution sediment coring study, a majority of the estimated and rejected data for the water-column monitoring program were still a result of dual GC column imprecision. TAMS/Gradient often qualified Station 2, 3; and principal congeners 4, 8, 10, 18, and 118 were qualified for a few SDGs. For SDG 185277, CDM qualified as rejected the positive results for BZ#2 in all samples due to the relative percent difference (RPD) between the results for both columns being greater than 90%. These results are not usable for project decisions.

B.5.3.2 Precision

Matrix Spike/Matrix Spike Duplicate Comparison

The analysis of matrix spike (MS) and matrix spike duplicate (MSD) samples can also provide valuable information regarding method precision relative to laboratory performance and specific sample matrix. The advisory limit for relative percent difference (RPD) of spiked congeners in a MS/MSD pair is 40%, and for nonspiked congeners, the precision criterion is 40% Relative Standard Deviation (RSD).

TAMS/Gradient noted MS/MSD exceedances for only 3 SDGs (190020, 183681, and 182249). Regarding principal congeners, the 40% RPD criterion was exceeded for BZ#8 for SDG 190020 and BZ#8, 18, 52, 101, and 118 for SDG 182249. Overall, MS/MSD performance for the water-column monitoring program was good.

Additional information on precision is also obtained from an evaluation of the field duplicate results, discussed (Subsection B.5.3.3).

B.5.3.3 Representativeness

Field Duplicate Results

Analysis of field duplicate samples provides an indication of the overall representativeness and precision of the sampling and analysis program. These analyses measure both field and laboratory precision; therefore, the results will likely have more variability than laboratory duplicates and MS/MSD samples, which only measure laboratory precision. Data validators used a 50% RPD criterion for evaluating field duplicate precision.

Field duplicate results for the principal congener for the dissolved water column samples are compared in Table B-1, and results for the principal congeners for the particulate water column samples are presented in Table B-2. The precision for the principal congeners throughout the water column program was good, except for SDG 187749 (Sample TS-005-0006), where all principal congeners had %RPD above 50% (typically 60% to 70%). A total of 33 congeners for TS-005-0006 were estimated (G) due to this problem.

B.5.3.4 Sensitivity

Blanks

An important data quality objective associated with the water-column monitoring program was to obtain detection limits as low as the analytical method could produce. One effect of this approach is to register low level blank contamination during the preparation and analysis of the water and particulates. As such, numerous congeners in all samples in all the SDGs required blank contamination qualifications. In general, TAMS/Gradient found blank levels lower for the water-column monitoring program than for the high resolution sediment coring study. TAMS/Gradient reviewed the distribution

of blank contaminants and found most contamination associated with the monochlorobiphenyls, particularly with BZ#2. Blank levels for BZ#2 typically ranged from 30 ppb to 70 ppb in extract; however, very high concentration of BZ#2 (542 ppb in extract) was detected in SDG 183681. The highest concentration of principal congener BZ#1 was 23 ppb in extract for SDG 185277, and for principal congener BZ#4 was 15 ppb in extract for SDG 182249.

CDM qualified results during data validations with a "B", which indicated that the result was within 5 times of the blank action level. TAMS/Gradient converted all "B" qualified results in the database to nondetect results due to uncertainty in this detection. Tables B-3 and B-4 summarizes the congener detects changed to non-detects for particulate and dissolved congeners, respectively.

Quantitation Limits

Evaluating dechlorination processes and modeling transport pathways of PCB congeners within the Hudson River water column necessitated obtaining low detection limits. TAMS/Gradient and Aquatec devised analytical methods to enhance lower detection limits. This, in part, required employing sample/extract cleanup methods to remove matrix interferences, and maximizing sample size when possible. For the water-column monitoring program, TAMS/Gradient defined optimum detection limits as follows:

Matrix	Homolog	Detection Limit
Particulates	Monochlorobiphenyl	2 µg/filter
	Dichlorobiphenyl through Hexachlorobiphenyl	1 µg/filter
	Heptachlorobiphenyl through Decachlorobiphenyl	1-2 µg/filter
Water (20 liters)	Monochlorobiphenyl	0.1 ng/L
	Dichlorobiphenyl through Hexachlorobiphenyl	0.05 ng/L
	Heptachlorobiphenyl through Decachlorobiphenyl	0.05-0.1 ng/L
Water (1 liter)	Monochlorobiphenyl	1.0 ng/L
	Dichlorobiphenyl through Hexachlorobiphenyl	0.5 ng/L
	Heptachlorobiphenyl through Decachlorobiphenyl	0.5-1 ng/L

Based on the results of the MDL study, TAMS/Gradient raised the detection limits for BZ#2 (a monochlorobiphenyl) significantly above these requirements (approximately a factor of 3). In addition, CDM selectively raised detection limits for BZ#2, 3 and 4 for SDGs 187749, 182249,

179045, 179191, 179067, 178104, and 187042 due to a lack of sensitivity during initial calibration (see Subsection B.5.3.1).

In general, achieving appropriate detection limits for the water column samples was not a problem. Whenever TAMS/Gradient noted raised detection limits, the affected samples contained high organic content; specifically the presence of PCBs. The relative ratio of congeners detected within each high-concentration sample remained reasonably consistent, therefore the raised detection limits for nondetect congeners did not affect data usability. For critical low level samples used for delineating the outer extent of contamination, or other PCB sources (*e.g.*, tributaries), Aquatec achieved adequate detection limits.

B.5.4 Usability - Principal Congeners

The 12 principal target congeners employed in the water-column monitoring program are key to delineating PCB geochemistry in the Hudson River. The following synopsis will provide data users with the strengths and weaknesses of the principal target congener data within the context of this study:

BZ#1. The reported results for BZ#1 met the data quality objectives of the program. Results for 4 samples were rejected due to dual GC column imprecision. Analytically, BZ#1 eluted as a single peak on one GC column and coeluted on the other GC column, which was acceptable for the purposes of this program. The detection limit goal was met for nearly all samples.

BZ#4. The reported results for BZ#4 met the data quality objectives of the program. Results for 12 samples were rejected due to dual GC column imprecision. Analytically, BZ#4 eluted as a single peak on one GC column and coeluted with BZ#10, another principal congener, on the other GC column. Data for both BZ#4 and BZ#10 were considered usable. The detection limit objectives were generally met, although some blanks ranged up to 15 ppb in extract and there were some sensitivity problems on occasion of the low-level standard. This did not affect data usability.

BZ#8. The reported results for BZ#8 met the data quality objectives of the program. Results for 38 samples were rejected due to dual GC column imprecision. The number of rejects for BZ#8 was significantly higher than that experienced for the high resolution sediment coring study. Analytically, BZ#8 eluted as a single peak on one GC column and coeluted with BZ#5 on the other GC column, which was acceptable for the purposes of this program. For some samples, the initial resolution criteria between BZ#8 and BZ#5 was not met, requiring associated data to be qualified presumptively present. This data should be considered usable. The detection limit goal was met for nearly all samples. Matrix spike results for BZ#8 further indicated that the method was successful.

BZ#10. The usability assessment for BZ#10 is similar to that for BZ#4. BZ#10 eluted as a single peak on one GC column and coeluted with BZ#4 on the other GC column. Data for both BZ#4 and BZ#10 were considered usable. Results for 10 samples were rejected due to dual column imprecision. In general, the detection limit objectives were met.

BZ#18. The reported results for BZ#18 met the data quality objectives of the program. Results for 12 samples were rejected due to dual GC column imprecision. Analytically, BZ#18 eluted as a single peak on one GC column and coeluted on the other GC column. In general, the detection limit objectives were met. Matrix spike results for BZ#18 further indicated that the method was successful.

BZ#19. Results for 40 samples were rejected due to dual GC column imprecision. The reported results for BZ#19 met the data quality objectives of the program. Analytically, BZ#19 eluted as a single congener on both GC columns. The detection limit objectives were met.

BZ#28. The reported results for BZ#28 met the data quality objectives of the program. Results for 3 samples were rejected due to dual column imprecision. Analytically, BZ#28 eluted as a single congener peak on both GC columns. In general, the detection limit objectives were met. Matrix spike results for BZ#28 further indicated that the method was successful.

BZ#52. The reported results for BZ#52 met the data quality objectives of the program. Results for 9 samples were rejected due to dual GC column imprecision. Analytically, BZ#52 eluted as a single congener peak on both GC columns. The detection limit objectives were met for nearly all samples. Matrix spike results for BZ#52 further indicated that the method was successful.

BZ#101. Data users should be aware that BZ#101 always coeluted with BZ#90. For reported results, all other QA/QC requirements were met, therefore should be considered usable. No samples were rejected. The detection limit objectives were met for nearly all samples. Matrix spike results for BZ#101 further indicated that the method was successful.

BZ#118. The reported results for BZ#118 met the data quality objectives of the program. Results for 43 samples were rejected due to dual GC column imprecision. The number of rejects for BZ#118 was significantly higher than expected for the high resolution sediment coring study. Analytically, BZ#118 eluted as a single congener peak on both GC columns. The detection limit objectives were met for nearly all samples. Matrix spike results for BZ#118 further indicated that the method was successful.

BZ#138. The reported results for BZ#138 met the data quality objectives of the program. No results were rejected. Analytically, BZ#138 eluted as a single congener peak on one GC column and coeluted on the other GC column. The detection limit objectives were met for nearly all samples. Matrix spike results for BZ#138 further indicated that the method was successful.

BZ#180. The reported results for BZ#180 met the data quality objectives of the program. No results were rejected. Analytically, BZ#180 eluted as a single congener peak on one GC column and coeluted on the other GC column. The detection limit objectives were met for nearly all samples. Matrix spike results for BZ#180 further indicated that the method was successful.

B.6 CONCLUSIONS

The PCB congener analytical chemistry program implemented by TAMS/Gradient for the Hudson River high resolution sediment coring study required the development and use of program-specific GC/ECD methodology in order to generate data meeting the data quality objectives of the program. A total of 281 dissolved, particulate, and whole water samples were analyzed for 126 target and non-target congeners. Considering the complexity of the program, TAMS/Gradient considers the outcome of the analytical chemistry program to have been successful.

A summary of the number of qualifiers applied to each PCB congener is tabulated in Tables B-3 through B-8. For the water-column monitoring program 35,726 congener measurements were recorded, of which 641 values were rejected. A 98.2% completeness rate was achieved for this program, which exceeds the 95% completeness goal. A breakdown of the rejected data per study follows:

Analysis	Data Points	Rejected Data	Completeness Ratio
Monitoring-dissolved	14,577	248	98.3%
Monitoring-particulate	14,663	288	98.0%
Equilibrium-dissolved	2,166	16	99.3%
Equilibrium-particulate	2,175	39	98.2%
Flow-averaged Event 7	381	6	98.4%
Whole water	1,764	44	97.5%
Total	35,726	641	98.2%

Although the completeness rate was higher for the water-column monitoring study than for the high resolution sediment coring study, the imprecision between GC columns remained a problem. A majority of the data that was either estimated or rejected was a result of dual GC column imprecision. With regard to the principal congeners, data rejected due to this problem included BZ#1 (4 rejects), BZ#4 (12 rejects), BZ#8 (38 rejects), BZ#10 (10 rejects), BZ#18 (12 rejects), BZ#19 (40 rejects), BZ#28 (3 rejects), BZ#52 (9 rejects), and BZ#118 (43 rejects).

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APPENDIX C

DATA USABILITY REPORT FOR NON-PCB CHEMICAL AND PHYSICAL DATA

C.1 INTRODUCTION

The usability discussion of the non-PCB chemical and physical data for the Phase 2A sampling and analysis programs is presented in this appendix and sorted by program and matrix type. The data usability reports assessing the PCB congeners for the high resolution sediment coring study and the water-column monitoring programs are provided in Appendices A and B, respectively. The high resolution sediment coring study and the confirmatory sediment sampling study data sets are evaluated together in Section C.2, and the review of the water-column monitoring program (water-column transects and flow-averaged sampling) results are presented in Section C.3. All chemical data associated with the collected field samples for these Phase 2A sampling and analysis programs have been validated (100% validation frequency) by CDM Federal Programs Corp. (CDM), TAMS, and/or Gradient. These data include the parameters listed in Table C-1.

CDM, TAMS, and Gradient performed data validation for the non-PCB parameters based upon the specific method criteria listed in the Appendices of the "Phase 2A Sampling and Analysis Plan/Quality Assurance Project Plan Hudson River PCB Reassessment RI/FS" (TAMS/Gradient, 1992, referred to in this report as the Phase 2A SAP/QAPP), and the USEPA Region II validation guidelines (USEPA, 1992), where applicable. TAMS/Gradient determined the usability of the data based upon an evaluation of the data validation reports in conjunction with historical or expected results, program data quality objectives (DQOs) as defined in the Phase 2A SAP/QAPP for the high resolution sediment coring study, the confirmatory sediment sampling study, and the water-column monitoring program. Additionally, TAMS/Gradient based the evaluation on usability on the intended use(s) of the data, consistency with other data sets (both internal, *i.e.*, from the Hudson River PCB Reassessment RI/FS and external, *i.e.*, historical data or data gathered from the literature), and professional judgment.

During the data usability assessment, final qualification of the data presented in the Hudson River project database were determined. In most cases, TAMS/Gradient maintained the qualifications added during validation and interpreted these qualifications in terms of the usability of the results for project objectives. In cases where the qualification of the data was changed from the validation actions, details of the technical justification for these changes, and the resultant usability of the data, are presented in this appendix for all non-PCB results generated in support of the high resolution, confirmatory sediment, water-column monitoring, and flow-averaged sampling programs.

An essential aspect of understanding the uncertainties of the Phase 2A chemical and physical data is understanding the significance of the qualifiers associated with the results. Initially, the analytical laboratories applied qualifiers to the results, then the data validators modified the qualifiers, as necessary, using established validation protocols from the USEPA Region II standard operating procedure (SOP) for data validation (USEPA, 1992), where applicable, the specific DQOs and quality control (QC) criteria established for the non-PCB tests in the Hudson River SAPs/QAPP (TAMS/Gradient, 1992), and professional judgment. All the analytical data (100%) collected in the Phase 2A programs were validated using validation protocols established by TAMS/Gradient and performed by CDM and TAMS/Gradient. The validation qualifiers were further modified, as necessary, during the usability assessment to direct the data users concerning the use of each result. Specifically, data were evaluated to determine compliance with the SAS request or the Phase 2A SAP/QAPP, adherence to the technical specifications of the analytical method prescribed, and achievement of precision and accuracy objectives of the analysis as measured by specific QC samples including laboratory control samples, matrix spike and duplicate samples, method and field blanks, field duplicate (split and co-located) samples, and calibration QC samples. The definition of the final qualification flags that appear in the database for non-PCB results are based upon USEPA data validation guidance (USEPA, 1992) and are listed in Table C-2. A complete list of result qualifiers, for both the PCB and non-PCB data, can be found in the “Qualify Table” of the project database.

The quality assurance/quality control (QA/QC) program included establishment of project DQOs, laboratory procurement and auditing and oversight, field sample auditing and oversight, method development and validation, and data validation. These QA/QC activities are described in the Phase 2A SAP/QAPP (TAMS/Gradient, 1992) and briefly summarized in the data usability

reports for the PCB congeners, which are provided in Appendices A and B. The pro-active approach to QA/QC, including on-site (field and laboratory) audits and implementation of corrective actions, as necessary, was successful in achieving the completeness goal of 95% for the collection of usable non-PCB data in support of these Phase 2A programs. In fact, for the results reported by TAMS/Gradient from laboratories procured specifically for the Phase 2A programs by TAMS/Gradient, less than 1% of the data were rejected, *i.e.*, considered unusable for project decisions. TAMS/Gradient considered several data sets generated by one of the SAS contract laboratories (Chemtech) as unusable due to method bias, high detection limits, and/or contamination. These unusable data include the SAS data for TON in the high resolution sediment coring study and DOC, TSS, and chlorophyll-*a* in the water-column monitoring/flow-averaged sampling programs. Nevertheless, data users have valid results for these parameters from the TAMS/Gradient contract laboratories; therefore, no significant data gaps were created by the loss of these SAS data.

C.2 HIGH RESOLUTION SEDIMENT CORING STUDY AND CONFIRMATORY SEDIMENT SAMPLE DATA

The high resolution sediment collection program, sampling procedures, analytical protocols and qualitycontrol/quality assurance requirements are presented in the Phase 2A SAP/QAPP and summarized in Appendix A of this report.

The non-PCB chemical and physical data for the confirmatory sediment sampling study include grain size (particle size) distribution, percent solids, total carbon (TC), total nitrogen (TN), total inorganic carbon (TIC), and reduction/oxidation potential (redox). In addition to these parameters, the high resolution sediment coring study provided for the collection and analysis of sediment samples for specific radionuclides (^7Be , ^{60}Co , ^{137}Cs), total organic nitrogen (TON), and weight-loss-on-ignition (WLOI).

C.2.1 Grain Size Distribution Data

Grain size distribution was determined for all confirmatory and high resolution sediment core sections to classify the type of sediment collected. These results are used in the interpretation of sediment PCB chronologies and degradation, particularly where important geochemical features correspond to changes in sediment texture. Due to the limited sample sizes for some of the high resolution sediment coring samples collected and the need to classify the entire grain size distribution on the same basis, a laser particle technique was used. Additionally, a subset of the sediment samples from both the confirmatory sediment sampling study and high resolution sediment coring study were measured using standard sieve/hydrometer methodologies for grain size distribution to provide a basis for comparison between the laser based particle analysis and the standard techniques.

Confirmatory sediment core and grab samples were collected and analyzed for grain size distribution by ATEC Associates using a sieve and hydrometer method (ASTM Methods D-421-85 and D-422-63, reapproved 1990) and by GeoSea Consulting, Ltd. using a combined sieving method (ASTM D-421-85 equivalent, to remove the particles greater than about 2 mm) and laser methodology (for the particle size distribution under 2 millimeters [mm]). The combined laser method was also used for the grain size analysis of the high resolution sediment coring samples. The grain size distribution results were validated for data package completeness, calibration verification, laboratory and field duplicate (co-located and split) results, and sample result verification. TAMS developed validation criteria for grain size distribution based specific method requirements, the project DQOs in the Phase 2A SAP/QAPP, and professional judgment.

Data were validated (by TAMS) and evaluated for usability by the TAMS/Gradient QA team. QC samples results (field co-located and laboratory split/duplicate samples) to evaluate representativeness and precision were obtained at a frequency of greater than or equal to the project DQO of 5%. The interpretation of the QC results and the accuracy and representativeness of the grain size data are evaluated in this section.

Gravel particles are typically not represented accurately in the collection of a small sample. This situation may result in a sample that is not representative of its general location and may cause a skewing of the weight distribution. Therefore, some of the grain size distribution results for

confirmatory sediment samples and small volume high resolution sediment coring samples were qualified, as described below.

C.2.1.1 Sieve/Hydrometer Grain Size Distribution Data

All of the confirmatory sample sieve/hydrometer data generated by ATEC is considered estimated (qualified J) due to the possible skewing of the distributions based upon the small sample sizes obtained for analysis. Note that for the initial distribution of the project database that five results were not qualified "J" in the project database, due to transcription errors, and should be considered estimated (qualified "J"). Limitations of the coring system used to obtain the samples, along with the need to obtain adequate sample volume for other analyses, limited the mass available for grain size analysis to about 250 grams (gm). The sieve/hydrometer method recommends minimum sample weights for the particle size analysis which are dependent upon the largest individual particle in the sample (*e.g.*, if the largest particle is 3/4" [19 mm; this was the median value for the 56 samples], a sample weight of 1000 gm is specified for determination of the greater than 2 mm [No. 10 sieve] fraction; 65 gm to 115 gm are required for analysis of the portion passing the No. 10 sieve). The laboratory was consistently able to generate adequate sample mass for the minus No. 10 sieve fraction (except in isolated instances where splitting a sample for QC analysis reduced the available sample quantity for each of the QC analyses), but not for the greater than 2 mm fraction. Therefore, a majority of the sieve/hydrometer data are estimated (qualified "J") due to the uncertainty in the representativeness of the gravel fraction which will also affect the percentages of the other fractions.

Overall precision of the sieve/hydrometer data were acceptable based upon laboratory split/duplicate and field co-located pair results. The ATEC sieve/hydrometer data are usable for general geotechnical classifications and ratios of fractions. Data users are cautioned that the data are questionable for other purposes due to insufficient quantities of the coarse fraction resulting in a potential bias in the gravel results, and, therefore, in the smaller size fraction results as well. The direction of this potential bias cannot be determined. Data users should note that, due to a minor transcription error, five results were not qualified as estimated (J) in the project database. As TAMS/Gradient considers all these data usable as estimated values, this omission does not affect the use of the data for project decisions.

C.2.1.2 Laser Grain Size Distribution Data

Due to the nature of the high resolution sediment coring study, only small volume samples (about 5 cc, or 10 gm) were available for grain size analysis from the same core interval analyzed for PCBs (since multiple analytical parameters were being aliquoted from a slice only 2 to 4 centimeters [cm] thick). The laser method utilized was selected specifically since it can be performed on small samples (a few grams); it does not require the large sample weights specified for the sieve/hydrometer method. In addition, the high resolution sediment coring locations were specifically selected based on anticipated deposition of fine-grained material; locations expected to contain significant sand or gravel were excluded from the high resolution sediment coring study. In addition to the small volume samples, a single large volume (200 to 500 cc, or about 500 to 1000 gm) sample was taken from a co-located core at each location (except Core 25). These large volume samples were taken from a larger interval (the top 8 cm) than the small volume samples, and no other analytical samples were taken from the same core and interval as the large volume grain size sample. The large volume samples provide a representative sample for complete grain size distribution analysis by the combined sieve/laser method. Small volume grain size sample data should only be used to represent differences among samples in the fine-grained fractions, *i.e.*, silt and clay. The accompanying large volume sample can provide a means to assess the presence of coarser fractions in the samples and therefore minimize the uncertainty in the overall distribution. The absence of gravel and coarse sand in the high resolution sediment samples supports the assumption that these sample locations are areas of fine-grained material and the use of the small sample volume to characterize the particle size distribution of these samples does not introduce any measurable bias.

The qualitative descriptions (gravel, sand, etc.) reported by GeoSea were based on the British Wentworth system, which is not comparable with the ASTM classification used in the United States and used for all other grain size data in this program. Therefore, TAMS converted the qualitative classifications of high resolution sediment coring and confirmatory sediment sampling grain size data on to the ASTM classification in order to make the GeoSea laser data comparable to other qualitative descriptions used in the Hudson River program. Laser grain size data reported by GeoSea in "phi" units were converted to millimeters (mm) using the equation $-\log_{10}(\text{diameter in mm})/\log_{10}2$.

The "mm" units were then assigned to the appropriate ASTM bins (sand, silt, clay). The updated classifications are included in the TAMS/Gradient database (Revision 3.1).

Additionally, the sieves used by GeoSea (their largest was 4.0 mm, corresponding to the No. 5 sieve) do not exactly correspond to the sieves used for ASTM classification, so there may be an overstatement of the gravel content inferred from GeoSea data, and a corresponding understatement of the coarse sand fraction, due to the necessity of including data from the 4.0 to 4.75 mm interval as gravel in the GeoSea data. This bias is not expected to be large; however, it will be further evaluated quantitatively during review of the low resolution grain size data analysis, in which the laboratory was explicitly requested to use both the 4.0 and 4.75 mm sieves.

The precision criterion originally specified in Volume 1 of the Phase 2A SAP/QAPP (TAMS/Gradient, 1992) for grain size distribution was based on the relative percent difference (RPD) of each individual particle size fraction. This criterion proved to be unworkable for the laser data, since particle size distributions were reported for 16 or more individual fractions (also referred to as "bins" for the laser data), some of which represented only a very small percentage of the total mass of the sample. Therefore, after a review of the initial grain size data was performed by TAMS, the criteria was modified to "percent similarity", rather than RPD. Percent similarity is a statistical test that compares the similarity of the two complete distributions and was developed specifically for the evaluation of laser particle size analyses (Shillabeer *et al.*, 1992). This criterion was used for the precision evaluation of all laser particle data generated for the Hudson River project and has been specified as the applicable criterion in the Phase 2A SAP/QAPPs developed for subsequent parts of the program.

Overall precision of the laser grain size data met acceptance criteria for a majority of the data (based upon the percent similarity of the distribution curves for laboratory duplicate pair results and field duplicate pair results). The mean correlation coefficient (r^2) of all the sample and duplicate pair results is 0.92, indicating acceptable agreement based upon linear regression statistics. The exceptions include one laboratory duplicate pair and five field duplicate pairs. These few data that did not meet the percent similarity precision criterion of greater than 80% represents 1% of the total number of sediment samples collected for laser grain size analysis. The variation in these duplicate results may be caused by the presence of significant amounts of organic material (*e.g.*, wood chips)

or gravel relative to the small sample size. The results may not be representative of the sample because the quantity of organic matter or gravel relative to the small sample size causes a skewing of the weight distribution. Therefore, the gravel fraction and the finer fractions may be improperly represented. Note, however, that less than 20% of the laser grain size samples contained gravel; therefore, the laser data were not significantly impacted. This was expected as a majority of the laser data were of the high resolution sediment core samples for which specific locations were chosen to represent the fine-grained material, *i.e.*, gravel was not expected in the samples.

Wood fragments and very low sample volumes, both of which may result in skewing of the weight distributions, accounted for the remainder of the laser data that were considered estimated. Based upon results presented in the main table of the project database, 110 confirmatory sample results (37% of reported results) and two high resolution sediment coring sample results (0.4% of reported results) for the laser grain size analyses were estimated (qualified J). All laser data are considered usable for project decisions for a completeness level of 100% for this parameter.

C.2.1.3 Summary Usability of Sieve/Hydrometer and Laser Grain Size Distribution Results

For the confirmatory sediment sampling study, the sample size limitations of the high resolution sediment coring study did not exist and confirmatory sediment samples were taken in areas where coarse grained material might be anticipated. Therefore, all confirmatory sediment samples analyzed by GeoSea and ATEC were large volume samples. Comparison of the 52 pairs (analyzed by both sieve and laser methods) indicates acceptable agreement on the gravel fraction (both methods averaged about 17% gravel); however, the average sand result was about 10% higher in the sieve data (the samples analyzed by the sieve method averaged about 78% sand, while the same samples analyzed by the laser method averaged about 68% sand). Conversely, the silt fraction was much lower in the sieve results (averaging about 4%) compared to the laser results (which averaged about 14% silt). Both data sets confirmed that there was little clay in the confirmatory sediment (grab and core) samples (0.6% to 0.9%).

The lack of comparability between the laser and sieve/hydrometer results was not unexpected. Due to the fact that the different methods measure different sedimentology properties

(sieve/hydrometer uses weight and the laser method uses volume), these data should not be considered equivalent and the results of the two methods cannot be used to assess the accuracy of the results. These data sets are not comparable; the data user is cautioned that only intra-method comparisons are valid.

In summary, the grain size data for the confirmatory sediment samples are usable for qualitative analysis, not quantitative analysis, due to the uncertainty in the gravel fraction that may cause a bias in the other fractions as well. For the high resolution sediment coring samples, the grain size data are usable for both qualitative and quantitative analyses. The laser analysis of the fine-grained material is probably a more accurate representation of the particle size distribution of the fraction under 75 micron (1 m) than the hydrometer analysis. Since gravel is not usually present, the potential bias due to small sample size is not a concern in the high resolution sediment grain size distribution data set.

C.2.2 Total Organic Nitrogen (TON) Data

Total Organic Nitrogen (TON) is functionally defined as organically bound nitrogen in the trinegative oxidation state. The project objective for this measurement was to determine the importance of inorganic forms of nitrogen in the sediment and to help validate the use of the simple total carbon/total nitrogen (TC/TN) ratio as a replacement for the organic carbon/organic nitrogen ratio for the assessment of sediment. Thus, the main data use for TON results was to compare them to the TN results to evaluate the potential contribution of organic nitrogen to the total nitrogen data for the Hudson river sediments. Though the TON data are valid, with some qualifications as described below, they did not meet project objectives and are therefore unusable for comparison to the TN data. Details of the measurements and QA/QC results, including a comparison of TON and TN data, are presented in this section.

C.2.2.1 TON QA/QC Results

The TON results were validated for data completeness, holding times, calibration verification, laboratory and field blank and duplicate results, laboratory control sample results, detection limit results, and sample result verification based on the method requirements, USEPA Region II data validation guidelines, wherever applicable, the DQOs specified in the Phase 2A SAP/QAPP, and professional judgment.

A total of 207 sediment samples, of which 18 were field duplicates, plus 13 field blanks were collected and analyzed during the high resolution sediment coring study. Analysis was conducted by Chemtech through the USEPA SAS program. All samples were prepared for TON analysis using "Standard Methods for the Examination of Water and Wastewater" (Standard Methods) (18th ed.) semi-micro Kjeldahl Method 4500-N_{org} and analyzed by USEPA "Methods for the Chemical Analysis of Water and Wastes" (USEPA, 1983) Method 351.3. The reported data measure Total Kjeldahl Nitrogen on a sample from which the ammonia has been removed prior to analysis. Therefore, the resultant value is considered, functionally, TON. Data are reported on a dry weight basis using units of mg/kg. The reportable quantitation limit for these sediments is 40 mg/kg. No TON data were rejected during data validation.

Field and laboratory precision of TON measurements were acceptable. Field co-located samples were collected at a frequency greater than the project DQO of 5% and laboratory duplicates at a minimum frequency of 5% . Although two of the 18 field duplicate pairs did not meet precision criteria defined in the Phase 2A SAP/QAPP and the USEPA Region II guidance (100% RPD for soil/sediment) for data validation (USEPA, 1992), the majority (16 of 18 pairs) showed acceptable precision.

Though the duplicate precision results indicate that the sample aliquots collected were reasonably representative of the sediments from specific locations of collection, the representativeness of some samples collected for TON may have been compromised due to low percent solids content. Half of the TON results were considered estimated, *i.e.*, qualified "J" or "UJ", due to low solids content of the samples ranging from 20% to 49.5%. It is difficult to obtain a

representative aliquot for analysis of a sample with low solids content. This may effect the representativeness and precision of the TON results. However, based on a review of the precision for the percent solids measurement (the average RPD for % solids duplicate pairs was 9.0%) and that the majority of the field co-located pairs met project-specific precision criteria, shows that the potential effect of the low percent solids is not a significant quality issue.

Accuracy, as measured by holding times, calibration QC (initial and continuing calibration checks and blanks), method blanks, and matrix QC (matrix spike samples) met acceptance criteria as set forth in the SAS request. Sensitivity of several results were compromised due to observed field blank contamination. Due to a communication problem among the involved parties (SMO, RSCC, TAMS, and Chemtech), the laboratory only analyzed two of the 13 field blanks. Both of the field blanks (but none of the laboratory blanks) exhibited low level contamination (blank concentrations of 0.6 and 1.0 milligrams/liter (mg/L), which correspond to sediment concentrations of 239 and 416 milligrams/kilogram [mg/kg], respectively). The source of the contamination could not be determined during the data review/data validation process, although it may be attributable to the water used for the field blanks (which was not the same as the water used by the laboratory).

Due to the observed field blank contamination, some results were negated during validation. Initially, detections were reported for all sediment samples. As a consequence of data validation, 43 results (21%) were changed to not detected, *i.e.*, qualified "U", with an elevated quantitation limit due to the field blank contamination. These samples are associated with the only two field blanks analyzed, which had been found to be contaminated. Since the remaining samples have no associated field blank data, they are considered estimated, *i.e.*, qualified "J", due to the potential for field contamination.

C.2.2.2 Comparability of TON to TN

Agreement between the TON data as reported by Chemtech and the TN data reported by LDEO (discussed below in Section C.2.3) is not acceptable. Most TON results reported by Chemtech were typically in the 250 to 700 parts per million (ppm) range, although higher values (1000 to 3000 ppm) were reported from the first two cores (HR-001 and HR-002). With the exception of most of the Core 1 samples, the TON data are consistently lower than the TN data, usually by a factor of

three to ten, despite the fact that a potential high bias is suspected in the TON data. These data (TON and TN) have been plotted together, and a regression analysis was performed. The slope of the fit, which ideally should be 1.0 (based on the assumption that most of the nitrogen in the sediments is organically bound) was less than 0.1, and the correlation coefficient (r^2) was also poor (r^2 about 2×10^{-5} for all data, and r^2 about .05 for TN less than 0.1%). The drop-off in reported TON values in Cores 3 through 28 (compared to the TON values reported for Core 1, and to some extent, Core 2) was also not consistent with the TN data.

The difference between the TON and the TN was significant and though the TN correlated well with the TC, the TON did not. The methods for TON do have interference problems from high organic contents, high inorganic salts, and the type of catalyst used in the preparation. All these interferences can cause a potential low bias in the TON results. Though TAMS/Gradient considers all the TON results as valid based on method compliance, some with qualification as stated above, these results are not comparable to the total nitrogen (TN) results determined by LDEO. The TON results are not usable for comparison to other data sets (including the TN data generated for this project by LDEO) or for evaluating the contribution of inorganic nitrogen to the TN value in the sediments.

C.2.3 Total Carbon/Total Nitrogen (TC/TN) Data

The data uses for the TC/TN results include: using the TC as a measure for either potential PCB contamination or potential adsorption of PCBs to establish a relationship between total organic carbon (TOC) and PCB contamination; and to use the TC/TN ratio to indicate the presence of wood material in a sediment sample which, in turn, could be used as an indication of relative measure of potential PCB contamination in the sediments based upon the historical association of wood cellulose in the Upper Hudson with high levels of PCB contamination. TAMS/Gradient considers 94% of the sample data planned for TC/TN in Phase 2A to be usable to meet these project objectives.

A total of 250 confirmatory sediment sample results and 457 high resolution sediment core sample results were provided by Lamont-Doherty Earth (formerly Geological) Observatory (LDEO) for TC/TN analyses. The analytical method used was adapted from a non-routine method developed for low-volume samples (small sample mass) and is described in Appendix G of the Phase 2A

SAP/QAPP (TAMS/Gradient, 1992). The samples were dried and pulverized prior to analysis. An additional 40 samples were not analyzed due to the fact that the samples were ungrindable after drying. Six results for TN and one result for TC were rejected during validation as unusable. Therefore, confirmatory sediment analytical completeness is 84%. This completeness level does not meet project DQO of 95%. Nonetheless, 100% completeness was achieved for TC/TN analyses in support of the high resolution sediment coring study. Overall completeness of 94% was achieved for TC/TN in Phase 2A sampling and analyses.

The TC and TN results were validated for data completeness, holding times, calibration verification, laboratory and field duplicate results, laboratory control sample results, detection limit results, and sample result verification. TAMS/Gradient developed validation criteria for TC and TN analyses based on USEPA Region II data validation guidelines, wherever applicable, the DQOs specified in the Phase 2A SAP/QAPP, and professional judgment.

Through review of the data and direct quality assurance oversight during sample analysis, TAMS/Gradient determined that overall precision and accuracy DQOs were met for the TC/TN. This was determined from QA/QC results including calibration criteria, initial and continuing calibration verification results, laboratory blank results, laboratory control samples, and duplicate precision specified in the Phase 2A SAP/QAPP. Although all TC/TN data are considered usable at this time, several method problems that required subsequent corrective actions or qualification of the data were discovered. Discrepancies or deviations from the quantitation and reporting criteria were found; these were corrected by the data validators, so that the final validated data reflect reporting and quantitation criteria and protocols as established for this project.

C.2.3.1 Total Nitrogen (TN) Data Usability

Total nitrogen results for the initial analytical batches for the confirmatory sampling program are considered estimated (qualified "J"), due to uncertainty in the quantitation caused by an instrument air leak. This problem persisted throughout the entire program and over 85% of the confirmatory TN data were qualified as estimated for this reason. In the high resolution TN data set, 100% of the data were similarly estimated (qualified "J"). (Data users should note that the project database (Version 3.1) contains a transcription error. Two TN results were left unqualified. These results should have been qualified as estimated ("J"). This omission does not affect data usability as TAMS/Gradient considers all estimated results to be usable for TN.) Additionally, six results (2% of the data reported) were rejected due to severe QA/QC problems and are unusable for project decisions and 40 sediment samples collected could not be analyzed because they could not be ground. A completeness of 94% for TN data in both the confirmatory sediment sampling study and high resolution sediment coring study was achieved.

Sensitivity met project requirements for TN, but required correction during data review. In accordance with the SOP for the method (TAMS/Gradient, 1992) the method detection limit was raised from 0.001% (10 ppm) TN to 0.02% (200 ppm) TN.

As previously discussed, the agreement between the TON results generated by Chemtech and the TN data from LDEO is poor. The TN values are three to ten times higher than the TON results. This difference may be due to a method bias in the TON data (see TON discussion). Since the cause of the discrepancy could not be determined, both the TN and TON data should be used with caution for any use other than evaluating relative concentrations within the individual data sets. These results are not comparable.

C.2.3.2 Total Carbon (TC) Data Usability

Some sediment samples exhibited a matrix effect for carbon. During the initial analysis, the affected samples were not completely combusted; therefore, the laboratory recombusted the sample and summed the first and second combustion results to obtain the total carbon value. TAMS/Gradient considers the affected data as usable, but estimated (qualified J) due to potential

uncertainty caused by matrix effects. This matrix effect was found mainly in samples collected in the Upper Hudson River during the confirmatory sediment sampling study. This problem was largely non-existent during the high resolution coring sediment study, as these matrix effects were observed in only about 2% of the high resolution sediment samples. In addition to the incomplete combustion problems, other TC data were qualified due to poor duplicate precision, reported values exceeding the calibration range, and lack of associated method blanks. Overall, 57% of the confirmatory TC data and 12% of the TC data from the high resolution coring samples were qualified as estimated. Only one TC result was rejected (in the confirmatory sampling program).

C.2.3.3 Summary of TC/TN Data Usability

TAMS/Gradient considers all unqualified and estimated TC/TN data to be usable. Due to the uncertainty associated with the estimated values, data users should understand that the uncertainty in the individual results carries through to derived data, such as the TC/TN ratio, which depend upon both these data sets. Data users should note that the project database did not always carry through the qualifiers to the calculated ratios. The seven rejected results (qualified "R") are not usable for project decisions. Additionally, 40 confirmatory samples collected could not be processed for analyses due to sample matrix. An overall completeness of 94% was achieved for TC/TN analyses in the confirmatory sediment sampling study and high resolution sediment coring study.

C.2.4 Total Inorganic Carbon (TIC) Data

The purpose of the TIC measurements was to characterize sediment and to determine total organic carbon (TOC) content of the sediment by subtraction of TIC from TC. The estimated (J) and unqualified TIC results are usable for these project objectives. Five TIC results were rejected (qualified R) and are unusable for the project. As for the TC/TN analyses, 40 confirmatory samples collected could not be processed for analysis due to the sample matrix. Therefore, the TIC completeness achieved for both the confirmatory and high resolution core data sets was 94%.

TIC analyses were performed on the same samples analyzed for TC/TN. This method, which was also developed for use on a small sample mass, is described in Appendix H of the Phase 2A SAP/QAPP (TAMS/Gradient, 1992). The TIC results were validated for data completeness, holding

times, calibration verification, laboratory and field duplicate results, laboratory control sample results, detection limit results, and sample result verification. TAMS/Gradient developed validation criteria for TIC analyses based on USEPA Region II data validation guidelines, wherever applicable, the DQOs specified in the Phase 2A SAP/QAPP, and professional judgment.

TAMS/Gradient found no routine QA problems during the oversight and data validation review of these data. The required QC, including initial and continuing calibration checks, duplicate precision, and sensitivity were met in most cases. Approximately 81% of the confirmatory TIC data and 96% of the high resolution sediment coring TIC data have been accepted without qualification; the remaining data considered were estimated for QC issues including low continued calibration verification (CCV) recovery, poor lab duplicate precision, or lack of a method blank associated with the samples. Five confirmatory TIC results were rejected due to severe QC exceedances. These results are unusable for project objectives.

TAMS/Gradient reviewed the TIC results, as compared to the TC results, to assess the overall contribution of TIC to TC. The TIC results were less than 2% of the TC values (less than 0.05% TIC absolute) in over 90% of the confirmatory sediment samples and less than 10% of the TC for 90% of the high resolution sediment samples (less than 0.8% TIC absolute). Based upon these results, TAMS/Gradient concluded that inorganic carbon was not a significant contributor of total carbon in most of the sediments analyzed. Therefore, for practical purposes, the carbon in the sediments analyzed is predominantly organic and the TC results can be considered equivalent to TOC, with some exceptions as indicated below.

During the high resolution sediment coring study, eight sample results exhibited significant TIC levels. These samples had TIC levels that were about 80% of the TC values. In other words, in these sediments, the inorganic carbon accounted for the majority of the total carbon in the samples. These eight samples were collected from the seven deepest samples from Core 20 and the deepest sample from Core 23. These samples were unique in several other ways, including relatively high percent solids content for river sediments (65% to 70%) and relatively low total carbon content (even in these samples the TIC was on the order of 1.5% to 2.0%) and low weight-loss-on-ignition (less than 2% WLOI). Samples from other phases of the Hudson River program, with the exception of some samples that were collected during the low resolution sediment coring study, were not

collected at depths from which this anomaly was likely to be present. TIC was not analyzed for the low resolution sediment coring samples. Therefore, TC data from the deeper low resolution sediment coring data should be reviewed in conjunction with percent solids and WLOI data, along with TC data from the other core intervals, to evaluate the possibility that this effect of a significant contribution from inorganic carbon to the total carbon load, may occur.

C.2.5 Calculated Total Organic Carbon (TOC) Data

The TC and TIC data were used to determine the contribution of inorganic carbon to the total carbon content in the sediments and calculating an organic carbon value by difference. TAMS/Gradient calculated total organic carbon (TOC) as the difference between the total carbon (TC) result and the total inorganic carbon (TIC) result for the same split or co-located sample for both the high resolution and confirmatory sediment sample data. There is no TOC data by an alternate (direct analytical) method to provide an independent basis for evaluating this derived value in sediments. Data users should note that though the TOC calculated values were not qualified in the project database, any uncertainty already described in the TC or TIC data for some samples (estimated results qualified "J"), is carried over into the calculated TOC result. The single rejected TC result in the confirmatory sediment data set was not used and therefore a TOC value does not exist for this sample.

Since the TOC data is derived, these data were not formally validated as such; however, the analyses on which the calculation is derived - TC and TIC - were formally validated. The calculated TOC achieved the same percent completeness as the component analyses (94%). TAMS/Gradient considers all calculated TOC results as usable for the project objectives. As noted above, for the purposes of this program, TC and TOC (in sediment) are sufficiently similar to be used interchangeably for all the confirmatory sediment and all but eight high resolution sediment coring sample results.

C.2.6 Weight-Loss-on-Ignition Data

The objective of collection of WLOI data was to use the WLOI as an estimate of TOC. The WLOI data covered by this section of the report consists of 457 analyses performed by LDEO on

sediment samples from the high resolution sediment coring study. WLOI represents the determination of weight loss *via* combustion at a specified temperature (375°C) of previously dried sediment or of non-filterable suspended solids retained by a glass-fiber filter. TAMS/Gradient defined the WLOI combustion temperature at 375°C so that the data generated would be comparable to historical data combusted at this temperature. The analytical procedure used for determination of WLOI is described in Appendix F of the Phase 2A SAP/QAPP.

CDM validated the WLOI results for data completeness, holding times, calibration verification, laboratory and field duplicate results, laboratory control sample results, detection limit results, and sample result verification. TAMS/Gradient developed validation criteria for WLOI analyses based on USEPA Region II data validation guidelines, wherever applicable, the DQOs specified in the Phase 2A SAP/QAPP, and professional judgment. In general, all data met the project QA/QC requirements for accuracy, precision, and sensitivity (detection limits).

The WLOI data generated by LDEO for the high resolution sediment core samples represent a consistent and accurate data set and can be used for any appropriate analysis by data users. Over 90% of the WLOI data have been accepted without qualification. Although a few samples were reported to have TC values greater than the WLOI value, these samples without exception had high TIC concentrations. The calculated organic carbon concentrations for these samples do not exceed the WLOI values, and therefore the results are considered reasonable. Overall, 100% completeness was achieved with 10% of the usable results considered as estimated values due to minor QC issues.

C.2.7 Radionuclide Data

The objective of collecting radionuclide data was to provide a means of establishing the sediment core chronology. Results for beryllium-7 (^7Be), cobalt-60 (^{60}Co), and cesium-137 (^{137}Cs) were generated to establish at least four radionuclide events expected to be seen in the sediments of the Lower Hudson and three in the sediments of the Upper Hudson. Based upon QA oversight during analysis and review of radionuclide calibrations, data packages, and data validation reports, TAMS/Gradient considers all the ^7Be , ^{137}Cs , and ^{60}Co data generated for the high resolution coring program as usable for these project objectives. The achieved completeness was 100%.

Radionuclide analyses were performed by LDEO and Rensselaer Polytechnic Institute (RPI) using the gamma spectrometry method in Appendix L of the Phase 2A SAP/QAPP and the QA/QC protocols defined in the Phase 2A SAP/QAPP (TAMS/Gradient, 1992). Dried and homogenized sediment aliquots were analyzed for the three principal radionuclides. For the high resolution sediment coring study, a total of 468 sediment sample results for ^{60}Co , ^{137}Cs , and 98 ^7Be results from core tops are presented in the project database. For a total of 1,034 radionuclide results in the project database, 130 (12% of the total) detected values were considered estimated (qualified "J") and 559 (54%) of the nondetected results were considered estimated (qualified "UJ") at the detection level. During data validation, a majority of the results were estimated for statistical counting error which contributes to the uncertainty in the accuracy of the concentration reported. As these radionuclide data are to be used to discern trends in a core, TAMS/Gradient considers all estimated data usable for project objectives. No radionuclide result was rejected (qualified "R") during validation or data usability assessment.

C.2.7.1 Radionuclide Data Validation

The radionuclide results were validated for data completeness, holding times, calibration verification, laboratory and field duplicate results, laboratory control sample results, statistical error, and sample result verification. TAMS/Gradient developed validation criteria for radionuclide analyses based on USEPA Region II data validation guidelines, wherever applicable, the DQOs specified in the Phase 2A SAP/QAPP, and professional judgment. In general, acceptable criteria were met for these QA/QC parameters with the exception of potential uncertainty in the accuracy of the data near the background concentrations or in cases of low activity counts.

The radionuclide method requires that activities (results) be corrected for background, blanks, the radionuclide branching ratio, the efficiency geometry of the detector, and for the radionuclide specific decay. TAMS/Gradient established data validation criteria for radionuclides to verify that sample results were accurate, included appropriate corrections, and accounted for background activities to verify that detected activities reported were statistically different from background. TAMS/Gradient established the statistical error evaluation to set criteria for the estimation and negation of activities based upon statistical error. Interpretation of radionuclide results as affected by the statistical error and background correction protocols are discussed in the following section.

C.2.7.2 Interpretation of Negative, Zero, and Background Activities for Radionuclides

TAMS/Gradient defined validation criteria for the statistical counting error for the radionuclide results. Specifically, all sample results with a statistical error (*i.e.*, counting standard deviation) of greater than 10% and less than 50% of the sample concentration (*i.e.*, the percent difference between the sample result and the statistical error in the sample result between 10% and 50%) were considered estimated (qualified "J") due to the uncertainty in the result based upon the statistical error. TAMS/Gradient considers these estimated results as statistically different from zero, with some uncertainty due to counting errors. In general, radionuclide results qualified "J" for counting statistics were reported at relatively low activities. Sample results that had statistical errors of greater than 50% of the sample result were considered to be nondetected with an estimated detection limit (qualified "UJ"). At the one sigma statistical error level, as calculated by LDEO, these values are not significantly different from zero.

In some cases, the procedure of subtraction of measured background counts from sample counts during the calculation of radionuclide concentrations resulted in negative concentration values, which should be considered zero for purposes of data interpretation. Zero and negative activities are not statistically different from background activity and therefore, have been qualified "UJ" regardless of the percent difference between the reported activity and the activity's statistical error (TAMS/Gradient, 1995). Low-level activities, for which the counting statistics show a high relative error (counting error of greater than 50% of the reported result) as described in the above criteria, are also considered not significantly different from background. These evaluations have been applied to the data during validation; therefore, some low-level positive values have been considered as not detected, *i.e.*, no activity, following data validation. Note that the statistical counting errors, representing one standard deviation, have been maintained in the database to give the data user additional information on the uncertainty of the reported radionuclide activities.

C.2.8 Percent Solids

Percent solids analysis was performed by LDEO by drying the samples at 110°C for two hours. The high resolution sediment core samples analyzed by Chemtech for TON were also subject to solids analysis (by drying overnight at 103°C to 105°C) in order to report the TON data on a dry weight basis. Visual (non-rigorous) inspection of the two solids data sets indicates good agreement, with a few exceptions. TAMS/Gradient recommends the use of the percent solids data from LDEO as the definitive results because they were performed solids on a large volume aliquot and therefore are likely to be more representative than the Chemtech solids determinations (which were performed on 2 to 3 gram aliquots of sediment samples submitted for TON analysis).

The slightly different temperatures used by Chemtech and LDEO for the solids determination are not expected to have any significance with respect to the comparability of the data. However, some samples analyzed for PCBs or for archiving were dried at significantly lower temperatures (35°C) and for significantly longer times; these solids determinations are not necessarily comparable to those determined at 105°C to 110°C.

Of 291 confirmatory sediment samples analyzed by LDEO for percent solids, 7 results (2% of the total) were qualified as estimated based upon poor field duplicate (co-located and/or split samples) precision. LDEO reported 457 results for percent solids of the high resolution coring samples. These results were not validated and were accepted as reported by the laboratory. TAMS/Gradient considers all LDEO percent solids data as usable. Therefore, a completeness level of 100% was achieved.

C.2.9 Field Measurements

Field measurements recorded during the high resolution sediment coring study and confirmatory sediment sampling study consisted of reduction/oxidation potential (redox or Eh potential) measurements of sediment pore water and the associated temperature at which the measurement was taken. The objective of this measurement was to serve as a rough indication of where sediment zones of reducing potential exist in the cores collected in order to correlate these

zones with areas of extensive PCB dechlorination. The field procedure is described in Appendix N of the Phase 2A SAP/QAPP (TAMS/Gradient, 1992). Redox measurements (in millivolts, or mv) of the pore water were taken by LDEO personnel (under TAMS supervision). Approximately 12 to 15 readings were recorded for each core.

TAMS reviewed the field notes and tabulated results to assess data usability. The data were properly recorded and appropriate calibration and measurement procedures were followed. Cores were typically stored on ice overnight prior to processing; therefore, the recorded temperature should not be interpreted as the ambient or in-situ sample temperature at time of collection. Notebook pages are neat and legible and the data can be reconstructed from the field notes. The temperature at which the measurement was taken is recorded in the field notes and also recorded on the tabulated (spreadsheet) data. One transcription error (between the raw field notes and the Excel spreadsheet; value for HR-022-1216P should be changed from "94 mv" to "-94 mv") was observed during the usability review. With the caveat that these are field data, the redox (Eh) data are of a quality consistent with the measurement system employed and as such are considered fully usable for the project objectives.

C.3 WATER-COLUMN MONITORING PROGRAM AND FLOW-AVERAGED SAMPLING PROGRAMS

The water-column monitoring program (January 29, 1993 through August 24, 1993) included samples analyzed for dissolved organic carbon (terminology used interchangeably with total organic carbon; see discussion below), total suspended solids, weight-loss-on-ignition, and chlorophyll-*a*. The flow-averaged sampling program included total organic carbon, total suspended solids, and weight-loss-on-ignition.

Two sets of "equilibration study" samples were taken during the water-column transect sampling program. The first - EQ1 - were taken concurrently with water-column Transect 2, and the second set were taken along with Transect 6. Although these samples were taken during the programs under consideration in this report, the "equilibration study" samples were taken solely to calculate the PCB distribution coefficient K_D . Therefore no specific discussion of these samples is in

this appendix. The water-column monitoring program sampling procedures, analytical protocols, and QC/QA requirements are presented in the Phase 2A SAP/QAPP and summarized in Appendix B.

C.3.1 Dissolved Organic Carbon (DOC) Data

The objective for this analysis was to provide a continuation of an existing database of DOC measurements that has been correlated with many historic water-column PCB analyses. The Phase 2A SAP/QAPP defined split samples for analysis by two different methods. The LDEO persulfate oxidation method adopted by RPI under contract to TAMS was performed to generate comparable data to the historic data set. The USEPA water quality method, performed by a USEPA SAS laboratory, Chemtech, was defined for generating a reference data set using a standard USEPA method (EPA Method 415.1; USEPA, 1983).

Dissolved organic carbon (DOC) is defined for this program as the total organic carbon analysis of a sample which was filtered in the field through a glass fiber filter. For the flow-averaged sampling program and the water-column monitoring programs, the terms "DOC" and "TOC" have both been used to describe this parameter, though functionally, it is *dissolved* organic carbon. The data evaluated in this section include a total of 136 water-column monitoring and flow-averaged samples analyzed by RPI using the persulfate method as defined in Appendix C of the Phase 2A SAP/QAPP (TAMS/Gradient, 1992) and 115 water-column monitoring samples analyzed by Chemtech using EPA Method 415.1. The samples analyzed by RPI and Chemtech are splits of the same field sample.

Note that though field blanks were collected and analyzed for the DOC sampling and analysis program, they are not considered as a reliable indicator of field contamination and are not reviewed in this data usability assessment. Justification for this approach is found in a memorandum from USEPA Region II, dated April 12, 1993, concerning the Phase 2A SAP/QAPP for the Hudson River PCB RI/FS (USEPA, 1993). In this memorandum, it states "Field (equipment rinse) blanks are not required for TOC field samples and should not be collected. Analyte-free water does not need to be analyzed for TOC. TOC should not be considered an analyte, but rather a water quality parameter."

C.3.1.1 DOC Results - RPI

The DOC data generated by RPI are usable with some cautions. All of the DOC data were qualified as estimated ("J") by the validator (TAMS/Gradient for SDG 001, and CCJM under subcontract to CDM for SDGs 002 through 008) for method blank and control sample deviations. Review of the validation reports and other information suggests that these deviations did not significantly compromise data quality. Laboratory and field duplicate results for DOC indicated generally good precision, with only one duplicate pair substantially exceeding the defined precision objective (38.9% RPD for Transect 4 Station 6 duplicate, exceeding the 20% maximum RPD objective).

Validators estimated some of the early water-column data due to exceedances of holding times, in some cases substantial exceedances of several months. Based upon method requirements for preparing the samples by persulfate oxidation, TAMS/Gradient consider these data usable because they were "fixed" in sealed tubes prior to being held for analysis. Persulfate was added to the sample aliquot and purged of all CO₂ with a stream of helium. The ampule was then sealed and heated to 90 C for 4 hours. It was this sealed ampule that was held, past holding times, prior to analysis.

TAMS/Gradient instituted several corrective actions during a laboratory audit of RPI. These included: 1) performance of method detection limit and blank water studies; 2) routine analysis of a verified DOC standard following daily calibration; 3) routine analysis of matrix spiked samples at a frequency of 1 in 20; and 4) requirement of adherence to holding time of 28 days from sample collection to fixing the sample in an ampule for DOC analysis. These corrective actions resulted in usable data generated, with the quantitation limit for DOC increased from 0.025 mg/L, as listed in the Phase 2A SAP/QAPP (1992), to 0.25 mg/L, based upon results of the MDL/blank studies. The increase in MDL did not affect data quality as DOC values were consistently in the 4 to 5 mg/L range, and even the suspect Saratoga Springs sample values were two to three times the revised MDL.

DOC values from Station 9 (Saratoga Springs, selected as a background sample location) were relatively low compared to those from other stations (typically 0.9 - 0.9 mg/L, as opposed to 4

to 5 mg/L for other stations). Although Saratoga Springs is expected to have low organic carbon content, it cannot be determined whether the low values for this station are representative of the actual values or are biased low due to matrix interference (floc formation suspected to be iron hydroxide) as observed in the TSS/WLOI aliquots. Therefore, TAMS/Gradient considers the Station 9 DOC data as estimated values that may be biased low.

In Transect 4, the sample collected from Station 7 (SW) also exhibited an anomalous low DOC value (0.94 mg/L). This value is in poor agreement with other DOC values from this transect, and also does not agree well with the three other DOC values obtained at this station (which ranged from 4.26 to 5.22 mg/L). It is therefore likely that this value is not representative of conditions at this station, but rather is an outlier. Station 7 was deleted from the water-column monitoring program after the fourth transect was completed.

The Station 12 (Hoosic) data from Transect 3 are not legally defensible due to contradictions in documentation and therefore in establishing the identity of samples labeled TW-003-0012 and -0012D. Review of the field logs, as well as the analytical results, suggests that 0012D is not a duplicate of 0012, but rather was taken three days later than 0012, during the spring thaw. However, the formal chain-of-custody documentation indicates that both 0012 and 0012D were taken at the same time and day (March 27, 1993).

Several results for the flow-averaged sampling are unusable due to suspected sample bottle contamination. Whereas DOC values determined for the flow-averaged samples range from 4.0 to 6.0 mg/L, four flow-averaged composites for the second sampling event showed DOC values significantly higher, *i.e.*, from 10 to 16 mg/L. The eight individual DOC samples that made up the composite value were then analyzed separately for each of these stations. These individual analyses show that, for each station, at least one anomalous high DOC result is present. For example, for Station 4, sample FW-208-0004 showed 118 mg/L DOC. This value is more than an order of magnitude higher than all other DOC results for the flow-averaged samples. The field crew noticed that some of the samples foamed when placed in the sample bottles. It is suspected that contaminated sample bottles were the cause of the extremely high DOC values. TAMS/Gradient recalculated the composite DOC for the affected flow-averaged sampling stations by deleting results

for the contaminated samples. Sample bottle storage and use protocols were improved after this event and no such anomalous results were observed in subsequent data.

Overall, the RPI DOC data reported as estimated (J) or reported unqualified are usable for project objectives as the DOC values obtained compare well with historical data. Several results were rejected as unusable due to bottle contamination. An overall completeness of 96% was achieved for the DOC results obtained in the water-column monitoring and flow-averaged sampling programs. This meets the project DQO of 95% completeness.

C.3.1.2 TOC Results - Chemtech

The DOC analyses performed by Chemtech using the USEPA method were validated by CDM. Though CDM found no problems which would render these data unusable, anomalous results were reported for several stations. For example, samples from Station 9 (Saratoga Springs) consistently had anomalous high results (in the 300 to 500 ppm range) for DOC. As spring water samples, the Saratoga Spring samples would have high inorganic carbon (as carbonate) concentrations; the inorganic carbon is supposed to be removed by acidification of the sample prior to analysis. The detection of high organic carbon concentrations in the Saratoga Springs samples suggests that the laboratory either did not perform the acidification step, or performed it inadequately. TAMS/Gradient considers all Chemtech DOC data as potentially biased high (due to inorganic carbon being reported as organic carbon). Chemtech data therefore represent a worst-case (maximum) value for organic carbon in the water-column. Since there are RPI data available for the same samples, and the persulfate oxidation method used to determine DOC did not have a high bias, TAMS/Gradient recommends that data users rely on the RPI DOC data set for project uses.

C.3.2 Total Suspended Solids and Weight-Loss-on-Ignition (TSS/WLOI) Data

The objective of collection of TSS and WLOI data was to associate these values with the suspended matter/dissolved phase distributions of PCB congeners and use these results to help model PCB transport and water-column concentrations under seasonal flow variations. The TSS and WLOI data evaluated include a total of 856 results reported by RPI for TSS collected for the water-column transect, flow-averaged sampling, and high-flow suspended matter studies; 111 water-column transect samples analyzed for TSS by Chemtech under the USEPA SAS program, and 418 samples analyzed for WLOI by RPI for all three studies. Both RPI and Chemtech performed TSS using USEPA Method 160.2 (USEPA, 1983). The material analyzed for WLOI is the dried matter retained on the filters from the TSS analysis; WLOI represents the determination of weight loss by combustion at a specified temperature (375°C) of the dried sediment or non-filterable suspended solids retained by a glass fiber filter.

C.3.2.1 Weight-Loss-on-Ignition Data

The historical WLOI data are reported for combustion at 375°C. For this reason, the Phase 2A SAP/QAPP specified that WLOI data for the Hudson River project be combusted at the same temperature. However, due to laboratory error, samples from the water-column Transect 1 were combusted at 450°C. In an effort to determine the effect of this method change, RPI performed the WLOI at two furnace temperatures (375°C and 450°C) for the remainder of the water-column monitoring program samples. TAMS reviewed 76 analytical pairs of results at both temperatures and found that the WLOI result at the higher temperature is consistently about 20% higher than that at the lower temperature. Using the two data sets, TAMS developed a correlation between the results at the two combustion temperatures to convert results at 450°C to the 375°C equivalent WLOI (refer to Figure C.1). TAMS calculated a factor of 0.8636 by forcing the regression of the two sets of results through zero. Therefore, data users can obtain a conversion of WLOI from 450°C to a 375°C equivalent by multiplying the result for WLOI obtained at 450°C by 0.864. This calculated WLOI value has an uncertainty of approximately 20%.

In addition, TOC was not analyzed for the water-column samples in Phase 2A, thus TAMS further developed a correlation between WLOI at 375°C and TOC from the sediment sample data

(refer to Figure C.2). Organic carbon content can be estimated (calculated) from WLOI data by the equation: $TOC = WLOI (375^0) - 0.611$.

Due to the uncertainty associated with the Transect 1 WLOI values after the application of the conversion factor, data users may consider eliminating these results from their interpretation if there are sufficient data from Transects 2 through 6 for their intended use.

Precision of the WLOI results a function of the sample size. For this analysis, sample size is the mass of dried suspended solids recovered in the TSS analysis. For the 1-liter samples, the WLOI values have greater uncertainty when the TSS results were less than about 2 mg/L. These results should be used with the understanding that they are estimated values. WLOI data are more reliable from larger volume samples (3 to 4 liters) and samples with higher TSS values, since the relative impact of the weighing error decreases with increased weight.

Due to the formation of a floc believed to be iron hydroxide, TAMS/Gradient considers unusable all TSS/WLOI data from Station 9 (Saratoga Springs). These results were rejected (qualified R).

C.3.2.2 Total Suspended Solids (TSS) Data

TSS analyses were also performed by Chemtech on samples from the six water-column monitoring sampling events. Reported field blank contamination is a significant data quality issue for this data set. TAMS validated and rejected (qualified "R") all TSS data from the first two transects because of field blank contamination. TSS contamination was detected at 5 mg/L in all three field blanks from Transect 3, which should have been cause for rejection of all, but three sample results (all data > 25 mg/L TSS), although no action was taken by the validator. The single TSS field blank submitted with Transect 4 was not contaminated and data were acceptable (except field duplicate pair qualified estimated for poor precision). No field blank was submitted with the fifth transect, so TSS data from Transect 5 were qualified as estimated. Variable contaminant levels (not detected at 1 mg/L to [detected at] 4 mg/L TSS) were reported in the field blanks associated with Transect 6.

The rejected data are completely unusable; it is further recommended that the remainder of the TSS results reported by Chemtech not be used due to the overall uncertainty and probable high bias of the results. Analyses for TSS performed by RPI are more reliable and TAMS/Gradient recommends that the RPI data be used as the definitive TSS results for the water-column transect. The Chemtech data have been eliminated from the main table of results in the project database.

C.3.2.3 Flow-Averaged Sample Results

TSS/WLOI data were generated from six flow-averaged sampling events from April 23 to September 23, 1993. Each event was a separate SDG; the data from the second event (SDG 010) were validated by TAMS/Gradient, and the remaining flow-averaged TSS/WLOI data were validated by CDM (Federal Programs Corp.). Analytical methodologies were the same as for the water-column monitoring analyses discussed above. For the flow-averaged WLOI analyses, RPI combusted all samples at 375° (as well as at 450°); therefore none of the WLOI data needs to be adjusted due to combustion temperature.

The TSS method used for these analyses (EPA method 160.2) has a detection limit of 4 mg/L, based on drying the material to a constant weight (defined as ± 0.5 mg) and using a 250 mL sample (the 4 mg/L is derived from two weightings each of 0.5 mg maximum error, or total error of 1.0 mg for 250 mL). The detection limit can be improved by increasing the aqueous sample volume, since the limiting factor is the mass of suspended matter retained on the filter. In order to obtain reportable results (*i.e.*, positive values greater than the detection limit), the sample volume was increased (approximately 1000 mL was filtered for the daily RPI TSS analyses; the composite (X09-000X) samples were typically 3500 to 4000 mL); the weight of suspended matter was greater than 1.0 mg for all samples except one. It should be noted that in some cases the data validator (CCJM) negated low reported values (less than 1.6 mg/L) for which the raw data showed that more than 1.0 mg of solids were retained; these values have been reinstated by TAMS/Gradient. Only reported results for which the mass of suspended matter was less than 1.0 mg have been considered to be non-detected (qualified "U" or "UJ").

The data set for the flow-averaged data includes individual (daily) analysis of samples, as well as a composite sample result, for each station (location). RPI performed a mechanical

composite (*i.e.*, poured aliquots of the eight individual samples to create a composite sample "9") and analyzed this composite as a sample. The data for the mechanical composite has been replaced, in the project database, by a mathematical composite. The mathematical compositing was performed during the data usability review by taking the eight individual TSS values for a flow-average transect and mathematically combining them using transect-specific volumes normalized to the flow rate for that particular sampling event. This mathematical composite is a more technically valid result than the mechanical composite for the following reasons:

1. For the mechanical composite, several of the individual TSS samples were out of holding times. This may introduce a low bias in the result.
2. Error may be introduced into the mechanical deposit because it is difficult to obtain a representative aliquot of the individual samples. Particles may start settling as the aliquot is being poured thereby introducing uncertainty in the representativeness of the sample aliquots that make up the mechanical composite. This may cause a low bias in the result.
3. A review of the flow-averaged data showed that some of the mechanically composite results were biased low, relative to the mathematically-derived composite result. For the several of the 15-day composites evaluated, the mathematically-derived TSS value was up to 29% larger than the composite, and averaged 15% higher. This is consistent with the direction of the bias expected if the mechanically derived composites were not representative in TSS for individual aliquots due to settling of suspended solids particles during the process of compositing. For Transect 3, data shows a significant low bias of the composites as opposed to the calculated flow-averaged value; the calculated values exceed the composites by over 28% for all four stations.

The values for flow-averaged Transect 3, day seven at Station 4 (FW-307-0004 at 19.24 mg/L TSS) and flow-averaged Transect 2, day seven at Station 4 for the field co-located sample (FW-207-0004 field co-locate at 18.09 mg/L) appear to be outliers. It is likely that sediment was disturbed during the collection of these samples. These values have been rejected (R), along with the WLOI

values for these samples, and the data are unusable. Therefore, the mathematical composites calculated for these stations include seven, rather than eight, individual TSS and WLOI values. The composite results were re-calculated during the data usability assessment and have been updated in the project database.

RPI performed three weighings as part of the TSS determination. In cases where there was a significant discrepancy between the driest weight and the other two weights, RPI performed a fourth drying cycle and weighing. This procedure was performed for some of the samples associated with the flow-averaged Transect 2. For affected samples, the TSS was re-calculated using the average of the four weights, rather than the driest weight. These re-calculations were performed during the data usability assessment and the corrected values are reported in the project database. The technical justification for these re-calculations include:

1. the laboratory noticed a problem with the consistency of the weights; therefore, they performed an additional weighing;
2. the average of the four weights will give a more representative TSS result than using the driest weight if there was a potential for inconsistency in weightings.

Affected data include flow-averaged Transect 2 for Stations 4, 5, and 8 for days 5 through 8, as listed below:

Station 2	Station 4	Station 5	Station 8
FW-205-0002	FW-205-0004	FW-205-0005	
FW-206-0002	FW-206		
FW-207-0002	FW-207		
FW-208-0002	FW-208	FW-208-0005	FW-208-0008
	FW-205-0004 FCC		
	FW-206-0004 FCC		
	FW-207-0004 FCC		

Notes: FCC =Field Co-located

These data are considered estimated (J) and are usable as estimated results. Several results were negated (U or UJ) for TSS due to blank contamination. Associated WLOI results were rejected (R) because if TSS is not detected, then the measured value for WLOI must be an analytical artifact or error.

C.3.3 Chlorophyll-*a*

The objective for this measurement was to collect reliable chlorophyll-*a* data as an important factor in defining the partitioning ratios of PCBs between dissolved and suspended matter phases. Chlorophyll-*a* data were obtained for water-column samples for the first three transects through the USEPA SAS contract laboratory, Chemtech. Although these data were "valid", these data are not useful due to the high quantitation limit reported by the laboratory. The reported detection limit for these samples (25 mg/L) exceeds the maximum expected concentration (on the order of 10 mg/L to 15 mg/L); therefore, to prevent possible inappropriate use or inferences being drawn from these data, they have not been included in the database.

Subsequently, Inchcape Analytical Testing - Aquatec Laboratories (Aquatec), under contract to TAMS, analyzed samples from water-column Transects 5 and 6 for chlorophyll-*a* using the more sensitive (spectrophotometric) method (10200-H.3), with a detection limit of 0.5 mg/L. Aquatec data were consistent with expected values with chlorophyll-*a* detected in all 27 samples at concentrations ranging from not detected at 0.5 mg/L to 20.0 mg/L (uncorrected). The method also provides for a correction to the chlorophyll-*a* calculation for pheophytin. Aquatec performed this correction and also reported this result (in the data as "corrected"). The corrected value is typically about 0.5 mg/L to 0.8 mg/L chlorophyll-*a* lower than the uncorrected value, although there are a few exceptions. TAMS/Gradient recommends that data users employ the corrected with the caution that any comparisons to data from other sources also be "corrected". TAMS/Gradient considers all the Aquatec chlorophyll-*a* data usable for project objectives. Only one result was estimated due to minor QC issue and 100% completeness was achieved for the Aquatec data.

C.3.4 Field Measurements

The objective of the field measurements, including pH, temperature, conductivity, and dissolved oxygen was to obtain measurements for standard indicators of water quality conditions. Field measurements, including pH, temperature, dissolved oxygen, and conductivity, were obtained during water column monitoring (including both the water column transects and flow-averaged sampling). A complete set of data was obtained. Due to concerns about the accuracy of some of the measurements, laboratory determinations of pH and conductivity were made subsequently to the field determinations. These field measurements are included in the database and data are generally considered usable, as discussed below.

C.3.4.1 Temperature

Temperature measurements were made concurrently with the determination of other parameters (pH, conductivity, and dissolved oxygen). The temperature measurements are used to correct the raw field and readings to a constant temperature (*i.e.*, 25° for conductivity). In the case of dissolved oxygen, the temperature measurements are used to determine the theoretical oxygen saturation concentration so that the data can be expressed as percent saturation. The temperature measurements were made using the same instrument used to measure the parameter of interest (*e.g.*, the YSI SCT meter was used to measure the temperature associated with the field conductivity measurements). While the accuracy of the measurements is assumed to be acceptable, there is some question as to their representativeness, especially for the first few transects where ambient and water temperatures were low (5°C and less). The field data indicate temperature variations of as much as 10°C between measurements of the same sample for different parameters, so there may be some question as to the accuracy of temperature-based corrections for such measurements. However, review of the field notes also suggests that this discrepancy may be due to differing time lags between sample collection and measurement of the three field parameters (*e.g.*, pH readings may have been taken 45 minutes after the conductivity measurement).

C.3.4.2 Dissolved Oxygen

Review of the dissolved oxygen readings indicate that they are reasonable and in the expected range (near 100% saturation for most samples; low values for Station 9 [Saratoga Springs]). Some measurements correspond to somewhat greater than 100% saturation (101% to 110%) in perhaps about 10% of the samples; this is not considered significant based on the intended use of the data (providing a crude estimate of gas exchange capability of various reaches of the river). The temperature associated with the dissolved oxygen meter is that measured by the instrument (YSI 51B) and is used to determine the saturated oxygen content of water at the measurement temperature. No barometric pressure or altitude correction has been made; the maximum elevation of any of the sampling locations (about 200 ft) introduces less than a 1% change in the saturated dissolved oxygen concentration. It is also of note that temperature-specific oxygen saturation concentrations vary by 1% to 2% depending on the reference, or the edition of the reference. The dissolved oxygen data in the database consist of the raw field reading and the temperature at which it was taken; it is not converted to percent saturation.

C.3.4.3 Conductivity

Conductivity measurements were made both in the field at the time of collection (using the YSI Model 33 S-C-T meter with YSI 3310 probe) and later in the RPI laboratory (using a Leeds and Northrup model 4959 meter and YSI 3417 probe). The RPI narrative indicates that the laboratory, as opposed to field, measurements are considered more reliable. It should also be noted that a Hudson-specific temperature correction was applied to the data; this correction factor is non-linear and results in a slightly higher correction being added to measurements below 25°C than the 1.9% per degree cited in Standard Methods (17th edition). (The Hudson-specific correction factor, based on Dr. Bopp's conductivity measurements taken at six different Hudson River tributaries, is $\text{Cond}_{25} = \text{Cond}_t e^{0.0223(25-t)}$, where t is the measurement temperature in °C.)

Water-column transect conductivity measurements. For the first two transects (in January and February, 1993), measurements at the northern stations (1 through 4) were conducted at low ambient temperatures (less than 5°C) and it has been reported that the instruments were not stable in the field. However, laboratory conductivity measurements were taken about 70 to 90 days after the samples

were collected (April 30 through May 10, 1993); a maximum holding time of 28 days is cited both in Standard Methods (APHA, *et al*, 1989) (17th edition) and Methods for the Chemical Analysis of Water and Wastes (MCAWW; USEPA 1983). Therefore, the laboratory conductivity data for these two transects cannot be considered reliable. A limited review of the data indicates generally good agreement ($RPD < 20\%$), even between data pairs analyzed months apart (Transects 1 and 2); agreement is better between data sets analyzed closer together (Transects 3 through 6). Review of the field data in conjunction with the laboratory data suggests that the field data from Transect 1, Stations 2, 3, and 4, are outliers (the scale of the readings may have been misread by a factor of 10); otherwise, the field data appear adequate. However, the data entered into the database are the laboratory data. The laboratory data were selected since measurements were taken at closer to the normal reporting temperature (25°C) and therefore a smaller correction factor had to be applied.

Flow-Averaged sampling conductivity. Agreement between the field and laboratory conductivity data was generally good, although an even-dependent bias was noted. All flow averaged conductivity measurements were made within the 28 day holding time (averaging about 5 days after collection), although inspection of the data suggests that agreement between field and laboratory data is related to how soon after sampling the laboratory measurements were made.

Conductivity for three of the flow averaged events (1, 3, and 6) were reviewed in detail. In event 1, the average RPD was about 8.5%, although for 25 of the 27 measurements, the laboratory results were higher than the field results (after correcting both sets to 25°C); the two exceptions where field data were higher were two of the three station 8 results. In event 1, laboratory analyses were conducted an average of about 6 days after sample collection; field sample analysis temperatures ranged from 5°C to 13°C . In Transect 3 (excluding Station 8), the average RPD was about 2.8%, with the field data being slightly higher than the laboratory results. In event 3, the average interval between field sample collection and laboratory analysis was less than one day, and field sample temperature averaged about 20°C . Station 8 results were much more variable; the average RPD for Station 8 was slightly more than 10%, with no consistent bias (laboratory results for Station 8 ranged from 9% less than the field results to 27.5% greater than the field results). During the flow-averaged sampling, the average RPD for all stations (2, 4, 5, and 8) was about 13%; however, during event 6, the field measurements were consistently higher than the laboratory

measurements (28 of 31 field measurements were higher than the corresponding laboratory measurement).

The available information on data quality does not indicate a strong reason to believe either the field or the laboratory flow-averaged data set is better than the other. However, for internal project consistency, the laboratory flow averaged conductivity data has been included in the database. The laboratory-measured data set for the flow averaged sampling events is slightly more complete for the laboratory conductivity data, although the field data includes conductivity measurements at the west wall of the Waterford bridge (Station 8) which were not included in the laboratory analyses. Data (in the database) from flow-averaged event 1 may be biased high (based on comparison to the field data); conversely, a low bias may be present in the event 6 data. No significant bias is suspected in the event 3 data. The direction of bias, if any, was not evaluated for flow-averaged events 2, 4, and 5.

The original objective of the conductivity measurements was to obtain general water quality parameter data. However, when the water-column transect sampling event began, it was discovered that the US Geological Survey had discontinued flow monitoring at the Waterford gaging station, leaving the project without flow data for this part of the Hudson River. Therefore, an attempt was made to assess tributary contributions to main stem flow by means of a dissolved solids balance, inferred from the conductivity data. These attempts were not successful; partially due to the imprecision/inaccuracy of the conductivity measurements, and also due to the fact that complete mixing of the tributary with the Hudson River had not yet occurred at the downstream sampling station where conductivity was being measured. (For example, the field conductivity measurements at Waterford illustrate that the Hudson was not fully mixed across its width at that location.)

C.3.4.4 pH

During the water-column transect sampling, measurements of pH were taken in the field; subsequent measurements of pH were also taken in the laboratory. During the flow averaged sampling events, only laboratory measurements of pH were made. Field and laboratory measurements were both made with a Hannah Model 9025 meter and PCI E1000 epoxy/gel combination electrode. There is general consensus in the literature that pH values of water can change within minutes, and that pH analysis should be conducted as soon as possible (within 2 hours, or less, depending on the source). During the water column transect sampling, the laboratory pH measurements were made at least three days after sample collection (and in some cases as much as 90 days later); therefore, the laboratory pH data for water column transect sampling are not usable. Only the field pH data, along with the temperature of measurement, have been entered into the database. The gel electrode utilized for the pH readings was selected due to its ruggedness; it does take longer to equilibrate (stabilize) than conventional KCl-filled electrodes. Field pH data measured when water temperatures were low (less than 10°C or so) may be less accurate and may be biased low if readings were taken before complete stabilization occurred. Due to the difference in temperature at which pH readings were taken (instrument temperature compensation circuitry does not account for all possible temperature-dependent pH effects), as well as the lack of confidence expressed in the field data in the case narrative, the pH data are considered approximate.

As indicated in the discussion above, pH data are meaningful only when measurements are made shortly after sample collection. There are no field (real-time) pH data for the flow averaged sampling events; laboratory measurements were made an average of five days after sample collection. Laboratory pH data measured 24 hours or more after sample collection are unusable except as qualitative indications of water quality (*e.g.*, approximately neutral; strongly acidic). Only measurements made on the day of sample collection are considered to have any quantitative validity; and even these data are considered estimated due to the time lag between collection and measurement. The only pH measurements made on the day of sample collection during the flow averaged sampling were from days 1, 4, 5, 7, and 8 of event 3. The remaining flow averaged pH data are not considered quantitatively usable. It should be noted that the laboratory pH data are not quantitatively usable within a single event, since holding times varied widely within events (*e.g.*, the pH measurement of day 1 during event 6 was made 13 days after collection; the measurement for day

4 was made 7 days after collection; and the measurement for day 7 was made one day after collection).

References

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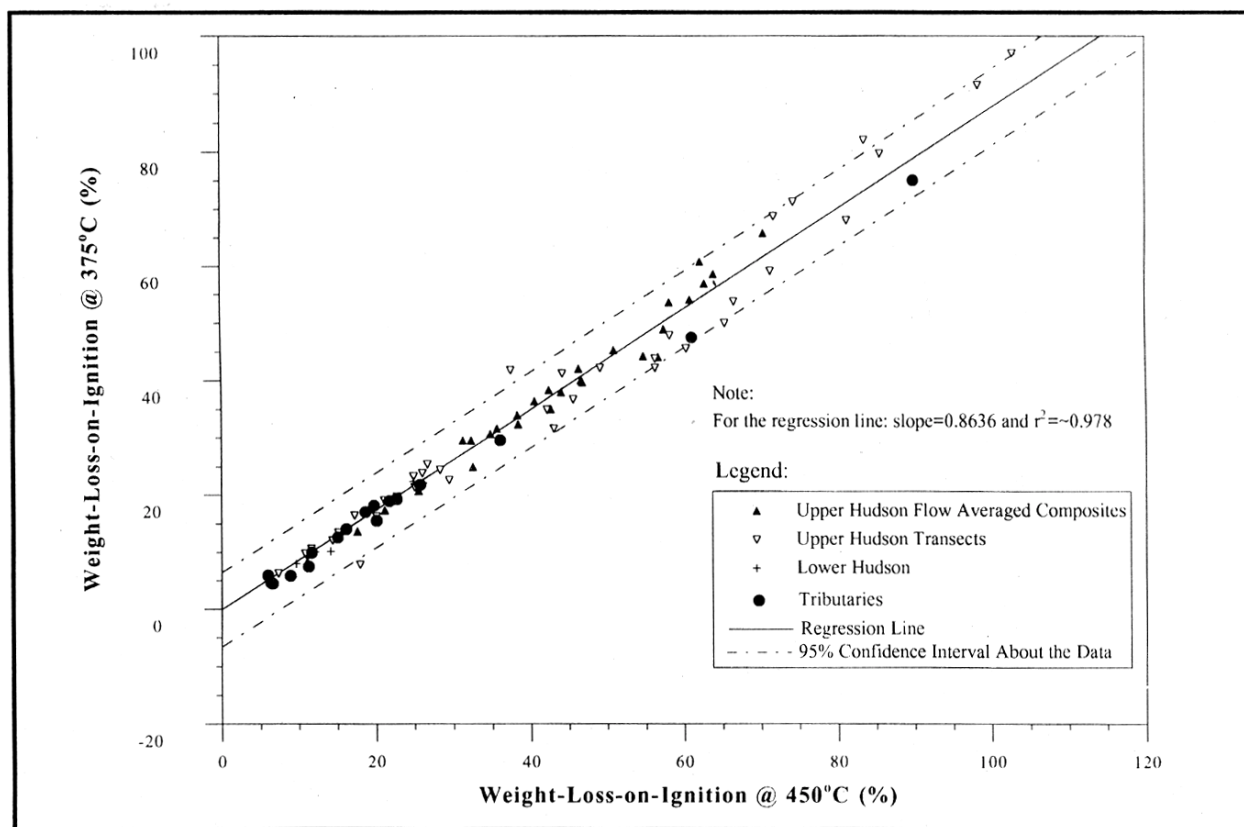
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Table C-1
Non-PCB Chemical and Physical Data Collected for the Phase 2A
Sampling and Analysis Programs

Parameter	High Resolution Sediment Coring Study	Confirmatory Sediment Sampling Study	Water-Column/ Flow-Averaged Sampling Program
grain size distribution			-
percent solids			-
weight-loss-on-ignition		-	
total carbon			-
total inorganic carbon			-
total nitrogen			-
total organic nitrogen		-	-
radionuclides (⁷ Be, ⁶⁰ Co, ¹³⁷ Cs)		-	-
dissolved organic carbon	-	-	
total suspended solids	-	-	
chlorophyll- <i>a</i>	-	-	
dissolved organic carbon	-	-	
field testing - redox	-		-
field testing - temperature, pH, conductivity, dissolved oxygen	-	-	

Table C-2
Qualifiers for Non-PCB Data

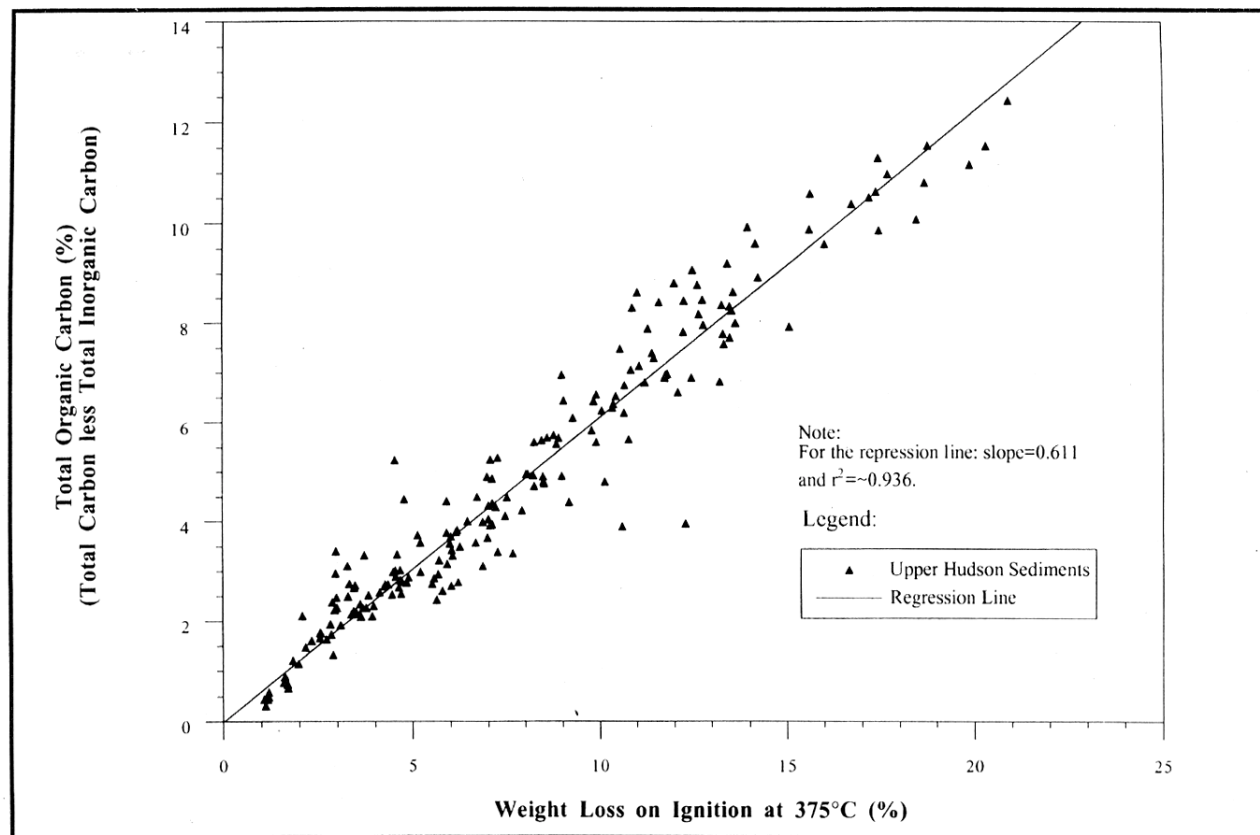
U -	The chemical or parameter was analyzed for, but was not detected above the level of the associated value. The associated value is the sample quantitation limit. The associated value is usable as a nondetect at the reported detection level.
J -	The associated value is an estimated quantity due to QA/QC exceedance(s). The estimated value may be inaccurate or imprecise. The associated value is usable as an estimated result.
UJ -	The chemical or parameter was analyzed for, but was not detected above the level of the associated value. The associated value is an estimated sample quantitation limit and may be inaccurate or imprecise. The value is usable as a nondetect value with an estimated detection level.
R -	The value (result) is rejected due to significant errors or QA/QC exceedance(s). The result is not usable for project objectives.



Source: TAMS/Gradient Database

TAMS/Cadmus/Gradient

Figure C-1
Weight-Loss-On-Ignition Comparison for Water Column Samples 375°C vs. 450°C



Source: TAMS/Gradient Database

TAMS/Cadmus/Gradient

Figure C-2
Comparison Between Weight Loss on Ignition at 375°C
and Total Organic Carbon for Upper Hudson High Resolution Core Sediments